DOCUMENT RESUME

ED 043 518 SE 009 801

| | |
|---|---|
| AUTHOR | Chernick, Cedric L. |
| TITLE | The Chemistry of the Noble Gases, Understanding the Atom Series. |
| INSTITUTION | Atomic Energy Commission, Oak Ridge, Tenn. Div. of Technical Information. |
| PUB DATE | 67 |
| NOTE | 53p. |
| AVAILABLE FROM | U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tenn., 37830 (free) |
| EDRS PRICE | EDRS Price MF-$0.25 HC Not Available from EDRS. |
| DESCRIPTORS | *Chemical Bonding, Chemical Reactions, *Chemistry, *Resource Materials, *Science History, *Scientific Research |
| IDENTIFIERS | Atomic Energy Commission |

ABSTRACT

The history of the discovery, isolation, characterization, production and use of argon, krypton, xenon, helium, and radon is followed by an account of early attempts to react them with other elements. The use of the electron shell theory of valence to explain their inertness and the reactions of chemists to the production of xenon compounds is described. The presently know n compounds of xenon and krypton are listed, and the use of molecular shapes of these compounds as determined by x-ray crystallagraphy and electron diffraction to test theories of chemical bonding is discussed. Illustrations, a short bibliography, and a film list are included. (AL)

# The Chemistry of
# the noble gases

U.S. DEPARTMENT OF HEALTH, EDUCATION & WELFARE
OFFICE OF EDUCATION

THIS DOCUMENT HAS BEEN REPRODUCED EXACTLY AS RECEIVED FROM THE PERSON OR ORGANIZATION ORIGINATING IT. POINTS OF VIEW OR OPINIONS STATED DO NOT NECESSARILY REPRESENT OFFICIAL OFFICE OF EDUCATION POSITION OR POLICY.

ED043518

U. S. ATOMIC ENERGY COMMISSION / Division of Technical Information

SE 009 801

## The Understanding the Atom Series

Nuclear Energy is playing a vital role in the life of every man, woman, and child in the United States today. In the years ahead it will affect increasingly all the peoples of the earth. It is essential that all Americans gain an understanding of this vital force if they are to discharge thoughtfully their responsibilities as citizens and if they are to realize fully the myriad benefits that nuclear energy offers them.

The United States Atomic Energy Commission provides this booklet to help you achieve such understanding.

Edward J. Brunenkant

Edward J. Brunenkant, Director
Division of Technical Information

**UNITED STATES ATOMIC ENERGY COMMISSION**

**Dr. Glenn T. Seaborg, Chairman**
**James T. Ramey**
**Wilfrid E. Johnson**
**Francesco Costagliola**

ED0 43518

# The Chemistry of the noble gases

by Cedric L. Chernick

CONTENTS


THE GASES THEMSELVES . . . . . 1
- Discovery . . . . . 2
- Occurrence and Production . . . . . 4
- Uses . . . . . 7

EARLY HISTORY . . . . . 10
- Attempts To Form Compounds . . . . . 10
- Why the Gases Are Inert . . . . . 11

PREPARATION OF THE FIRST XENON COMPOUNDS . . . 18

COMPOUNDS OF XENON . . . . . 23
- Fluorine-Containing Compounds . . . . . 23
- Oxygen-Containing Compounds . . . . . 28
- More Complex Compounds . . . . . 31

COMPOUNDS OF OTHER NOBLE GASES . . . . . 32
- Radon . . . . . 32
- Krypton . . . . . 32
- Helium, Neon, and Argon . . . . . 33

SHAPES OF MOLECULES . . . . . 33
- Solid State . . . . . 33
- Gas Phase . . . . . 35
- Predicted Shapes and Chemical Bonding . . . . . 37

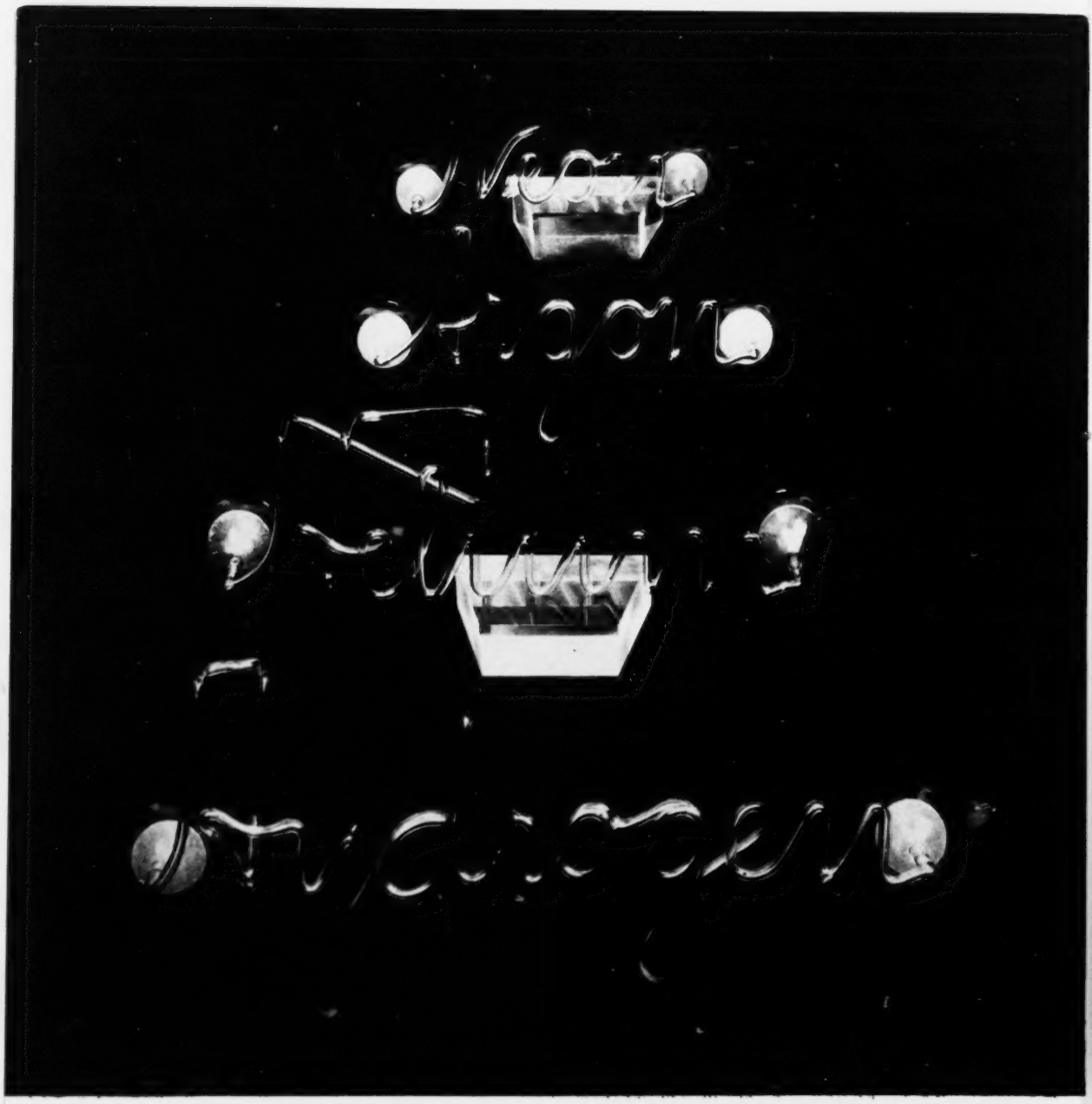
POSSIBLE USES . . . . . 43

SUGGESTED REFERENCES . . . . . 45



**United States Atomic Energy Commission**
**Division of Technical Information**

Library of Congress Catalog Card Number: 67-62972
1967



*These luminous Geisler tube script signs were made by E. O. Sperling, a glassblower at the National Bureau of Standards, for the 1904 Louisiana Purchase Exposition, St. Louis, Missouri. They are believed to have been the first examples of the use of the noble gases (and hydrogen) for display purposes. Each tube was filled by P. G. Nutting, an NBS scientist, with a sample of the appropriate gas obtained directly from Sir William Ramsay (see page 3). About 1930, the commercial use of neon tube signs began (see page 7), and since then neon signs have become commonplace the world over. Meanwhile, until 1962, at least, the noble gases remained among the most fascinating, most puzzling, and least known of all elements.*

# The Chemistry of
# the noble gases

By CEDRIC L. CHERNICK

## THE GASES THEMSELVES

If you've made up your mind that chemistry is a dull subject, and want to continue to think so, you should not read this booklet. It will only upset your comfortable conviction. If that should happen, it will be quite traditional, by the way, because information about the "noble gases" has been shattering cherished beliefs with remarkable consistency for some years now.

For over 60 years the 6 gases helium, neon, argon, krypton, xenon, and radon were the confirmed bachelors among the known elements. All the other elements would enter into chemical combination with one or another of their kind, irrespective of whether they were solids, gases, or liquids in their normal state. Not so helium, neon, argon, krypton, xenon, and radon. They were chemically aloof and would have nothing to do with other elements, or even with one another.

This behavior earned them a unique position in the Periodic Table of the Elements and they were called names like the "inert gases" or the "noble gases".* They were also labeled the "rare gases", although helium and argon are not really "rare".†

The inability of these gases to form chemical compounds was, until 1962, one of the most accepted fundamentals in

*"Noble" by reason of their apparent reluctance to mingle with the common herd of elements.

†Xenon, however, is the rarest of all stable elements on earth.

chemistry. Then along came some scientists with what Philip Abelson, editor of the magazine *Science*, later called "a germ of skepticism". In the space of only a couple of months all the dogma relating to the inertness of xenon was overthrown—it had definitely become a "joiner". Radon and krypton began "mingling" chemically soon thereafter and, although the other three gases are still holding out, the damage to a firmly cherished belief was done.

Table I
ABUNDANCE OF NOBLE GASES IN AIR AT SEA LEVEL

| Element | Symbol | Parts per Million (by volume) |
|---|---|---|
| Helium | He | 5 |
| Neon | Ne | 18 |
| Argon | Ar | 9430 |
| Krypton | Kr | 1 |
| Xenon | Xe | 0.1 |
| Radon | Rn | $6 \times 10^{-14}$ |

Some idea of the excitement these discoveries caused among scientists can be gleaned from the fact that, less than a year after the first discovery of a xenon compound was announced, a conference on "Noble Gas Compounds" was held at Argonne National Laboratory near Chicago. Some 100 scientists discussed work they had done in the field, and almost 60 made formal reports! The proceedings of that meeting filled a 400-page book entitled *Noble Gas Compounds.** Not bad, considering that just a short time before not even *one* noble gas compound was known.

This booklet will attempt to show how these gases lost their bachelorhood, and why today they are called "helium group gases" or "noble gases" instead of "inert gases".

## Discovery

The first indication of the existence of an inert constituent in the atmosphere came in 1785 when Henry Cavendish† found that he could not convert atmospheric nitrogen com-

*Edited by H. H. Hyman. See Suggested References, page 45.

†The great English chemist and physicist who also discovered hydrogen.

pletely to nitrous acid. He concluded that, "If there is any part of our atmosphere which differs from the rest ... it is not more than 1/120 part of the whole". This result was apparently forgotten or neglected, and the problem arose again in studies on the density of nitrogen in the early 1890s. At that time Lord Rayleigh* discovered that nitrogen obtained by removal of the then known gases from an air sample, or "atmospheric nitrogen", was denser than nitro-

*Sir William Ramsay*

gen prepared by chemical means—that is, "chemical nitrogen". A number of theories were advanced for the discrepancy in the densities of the nitrogen samples from the two sources. Either the "chemical" nitrogen was too light, or the "atmospheric" nitrogen too heavy, because of the presence of other gases. In 1894, however, Lord Rayleigh and William Ramsay† showed that the "atmospheric" nitrogen was a mixture of nitrogen and a heavier, previously undiscovered, gas. This gas turned out to be a new element that was given the name "argon", on account of its chemical inactivity (from the Greek word, *argon*, meaning inactive, idle).

---

*John W. Strutt, who inherited the title Lord Rayleigh, was director of the Cavendish Laboratory at Cambridge University in England when he did this important work. He is almost always referred to by his title.

†Ramsay was a Scots chemist who was knighted in 1902. He received the 1904 Nobel Prize in chemistry for his discoveries of noble gases. Lord Rayleigh received the 1904 Nobel Prize in physics in recognition of his nitrogen studies with Ramsay.

The discovery of the other 5 gases followed rapidly; by 1900 they had all been isolated and identified. Ramsay and his assistant, Morris Travers, in continuing their research on argon made use of newly developed methods for liquefying gases. The earth's atmosphere consists mainly of nitrogen (78%), oxygen (21%), and argon (1%), which have boiling points sufficiently different (−195.8°C, −182.96°C, and −185.7°C, respectively) that they can readily be separated by fractional distillation of liquid air. As Ramsay and Travers improved their techniques, they found that they could obtain several more fractions when distilling liquid air. Three of these fractions contained elements never before isolated, namely, neon (Greek, *neos*, new), krypton (Greek, *kryptos*, hidden), and xenon (Greek, *xenon*, stranger).

Ramsay was also instrumental in discovering the existence of helium (Greek, *helios*, the sun). This element had been noted in the sun's spectrum as early as 1868, but was only isolated as a terrestrial element in 1895 when Ramsay obtained it by heating the uranium-containing mineral cleveite.* (The helium in this mineral was physically trapped and was not chemically combined.)

The final noble gas to be discovered was radon. In 1900 Friedrich Dorn, a German physicist, found that radium evolved a gas that he called "radium emanation". This gas was later given the name *niton*, but since 1923 it has been known as *radon*. All isotopes of radon are radioactive.

## Occurrence and Production

The atmosphere is our major source for neon, argon, krypton, and xenon, and these gases are now produced commercially as a by-product during fractional distillation of liquid air to produce liquid oxygen and nitrogen. Liquefaction of thousands of tons of air per day makes these 4 gases available in sufficient quantities for present needs.

Helium is the second most abundant element in the universe. About 76% of the mass of the universe, it is esti-

*This mineral is also known as uraninite; one variety of uraninite, pitchblende, is an important source of uranium for production of atomic energy.

mated, is hydrogen; helium makes up about 23%, and all the other elements together compose the remaining 1% of the mass. Helium is so light that it is continually escaping from the earth's atmosphere into interstellar space. The present concentration of helium in the atmosphere therefore probably represents a steady-state concentration, that is, the amount being released from the earth's crust is equal to the amount escaping from the atmosphere into space. The constant escape explains why there is so little to be found in our air. Helium *can* be obtained from the atmosphere in the same way neon, argon, krypton, and xenon are, but is more readily obtained from accumulations that have built up in the earth's crust.

This helium in the earth is continually being formed by radioactive decay.* All radioactive materials that decay by emitting alpha particles produce helium, since an alpha particle is nothing more than a helium nucleus with a positive charge. Most of the helium in the earth's crust comes from the decay of uranium and thorium.

The helium is obtained by tapping natural gas wells, which yield an average helium content of about 2%. Most of these helium wells are in an area within 250 miles of Amarillo, Texas, although small amounts have been found in natural gas elsewhere in the U. S. Since the early 1950s helium-containing gases also have been found in South Africa, Russia, and Canada. In other parts of the world the helium content of natural gases and mineral springs is too low to make separation commercially attractive.

The helium is recovered from the natural gas by an initial liquefaction that leaves only helium and nitrogen in gaseous form. Further liquefaction, this time under pressure, causes most of the nitrogen to condense and leaves helium of about 98% purity in the gas phase. This can be further purified by passing it through a liquid–nitrogen-cooled trap containing charcoal, which absorbs the remaining impurities.

The final one of our noble gases, radon, is obtained from the radioactive decay of radium. One gram of radium produces about 0.0001 milliliter of radon per day. (We should

*For more about radioactivity see *Our Atomic World*, and other booklets in this series.

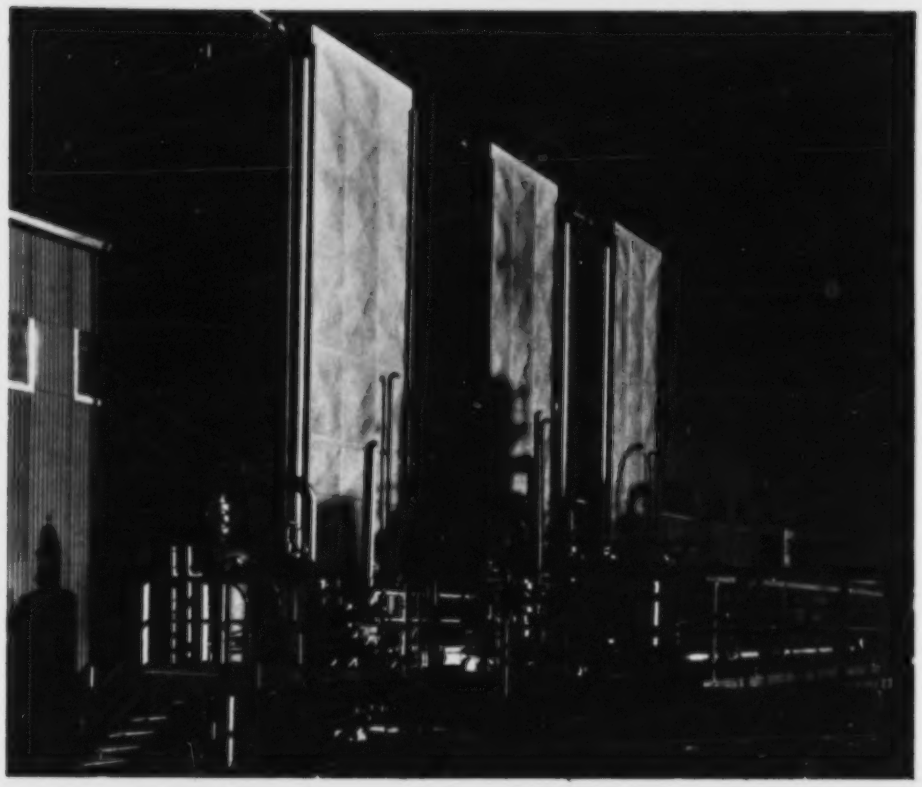


**Figure 1** *A U. S. Bureau of Mines helium plant in Keyes, Oklahoma, with the "cold boxes", or refrigerating units, in the foreground.*

keep in mind, however, that 1 gram of radium is a very large amount in terms of the total available.*) Radon has a short half-life (the commonest isotope,† coming from radium, is radon-222 whose half-life is 3.8 days), which means that about half the radon atoms will disintegrate in a little under 4 days. Since radium has a much longer half-life than that, about 1620 years, the amount of daughter radon in contact with the parent radium reaches a constant concentration. In other words the amount of radon being produced is balanced by the amount disintegrating, and as

*From the discovery of radium by Marie and Pierre Curie in 1898 until 1940 only about 1000 grams were isolated, and although production increased during World War II, it is doubtful whether there are more than 100 grams of pure radium available in the Western World today.

† Isotopes are the various forms of the same element. For a full definition of this and other unfamiliar words, see *Nuclear Terms, A Brief Glossary*, a companion booklet in this series.

soon as the primary source (the radium) is removed, the radon concentration begins to decrease because of its continuing disintegration. After 1 half-life (3.8 days) only half the radon remains; after a second half-life, ½ of that will have disintegrated, that is ½ of ½ or ¼; in a month there will be less than 1% left; and after $n$ half-lives the fraction remaining will be $(\frac{1}{2})^n$. The amount of radon one can isolate at any given time is, therefore, dependent on the amount of radium originally available.

A number of isotopes of the noble gases can be produced artificially, either directly by bombardment in a particle accelerator, or as the product of decay of an artificially excited atom, or by nuclear *fission*. The latter method is used for production of krypton and xenon in atomic reactors. Fission is a process in which a heavy atom splits to form 2 lighter atoms of approximately equal mass*; one or more neutrons and a large amount of energy also are released† simultaneously.

## Uses

Many of the uses of these gases are outgrowths of their inertness. The greater abundances, and hence lower costs, of helium and argon result in their use as inert atmospheres in which to weld and fabricate metals. The electrical and other properties of the noble gases make most of them ideal gases for filling numerous types of electronic tubes and in lasers. For this, the gases may be used singly or mixed with one or more of the others. Perhaps the best known use is in the familiar "neon" advertising signs. The glow produced by neon alone is red. The other gases produce less brilliant colors: helium (pale pink), argon (blue), krypton (pale blue), and xenon, (blue-green).

Helium, because of its lightness, finds use as a lifting gas for balloons and airships, although it is heavier than hydrogen. This weight disadvantage, however, is far overbalanced by the fact that helium is nonflammable. Recently,

*For example, if uranium-235 fissions, krypton-90 and barium-144, or xenon-140 and strontium-94 might be formed.

†For a full explanation of fission, see *Our Atomic World,* a companion booklet in this series.

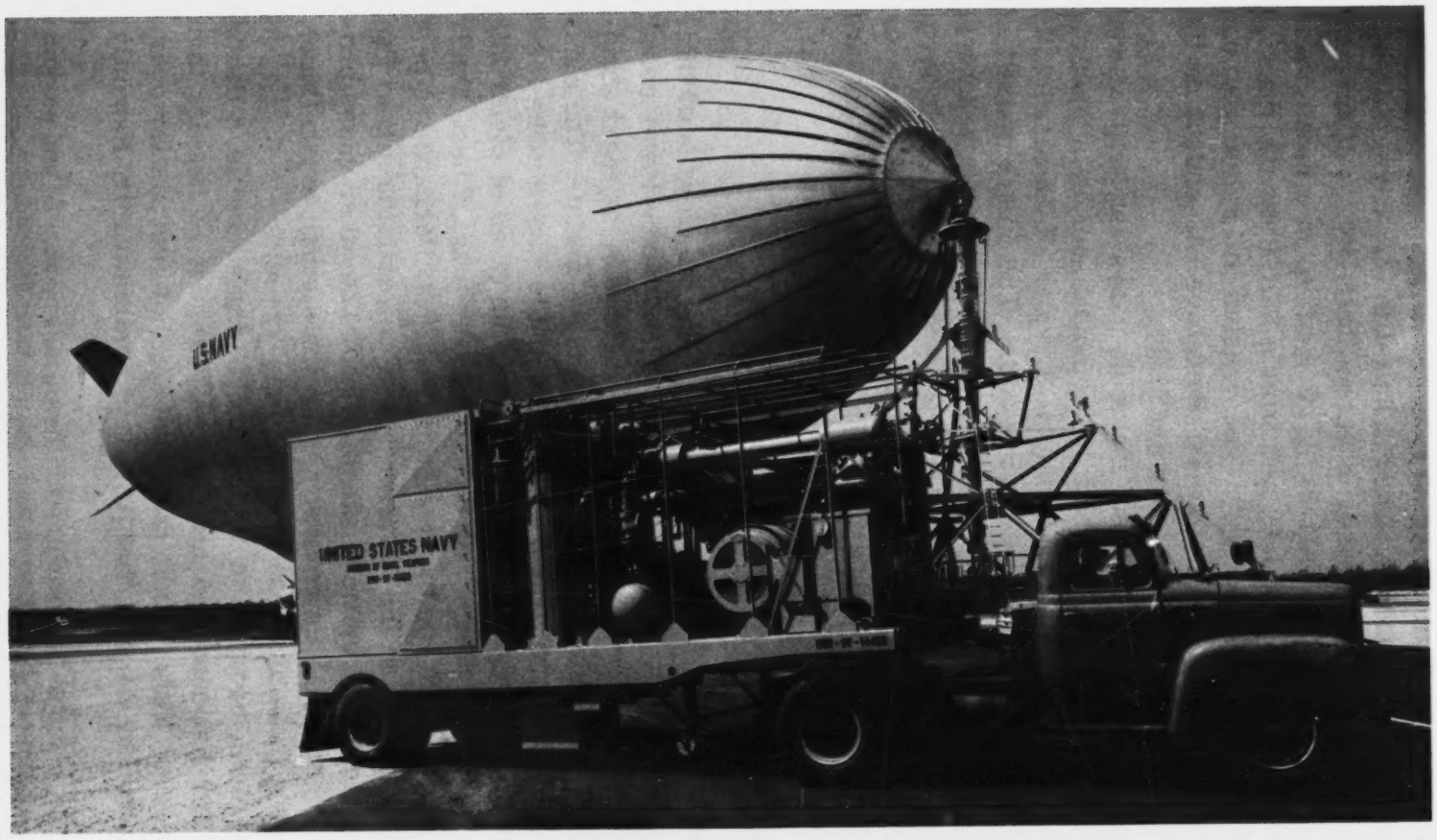



**Figure 2** *A mobile helium liquefier fills this U. S. Navy blimp.*

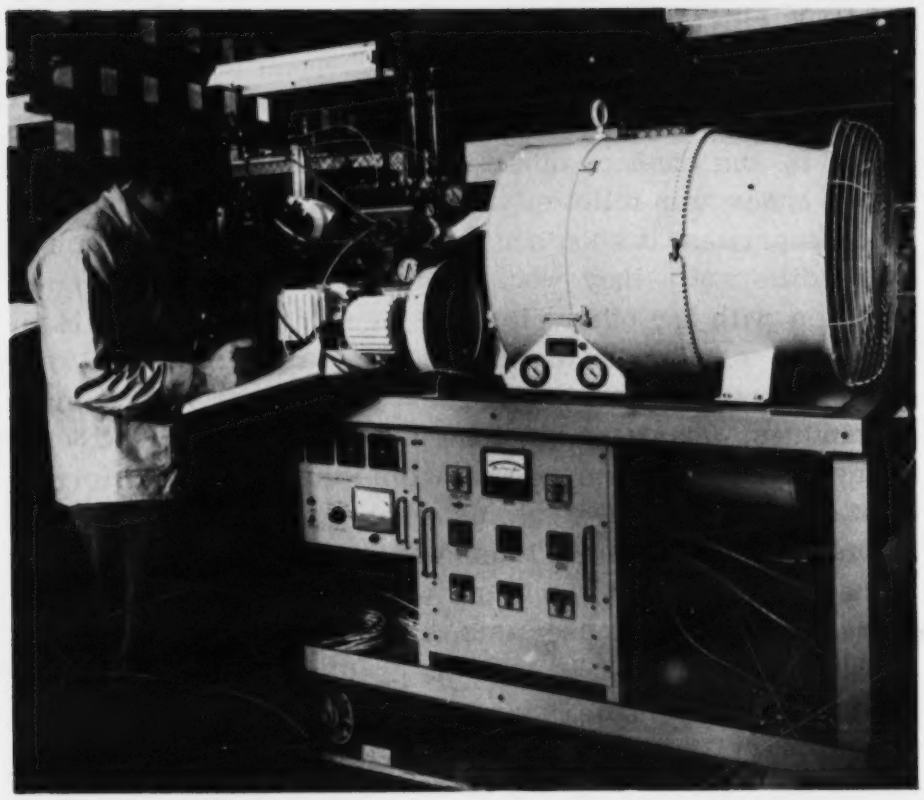


**Figure 3** *A technician checks a liquid-helium refrigerator prior to shipment. This unit is designed to cool masers and superconducting magnets used for space communication.*

helium has been used as a cooling medium in nuclear reactors, and it is also a diluent for oxygen in breathing systems for deep-sea divers. Helium being less soluble in the blood than nitrogen, the helium-oxygen mixture is preferable to normal air for persons working under pressure, since its use tends to prevent "the bends", a serious condition caused by gas bubbles in the body fluids and tissues. Liquid helium, which is the only substance that will remain liquid at temperatures close to absolute zero (−273°C), is finding increasing use in low-temperature physics—*cryogenics.** Radon has been used as a source of gamma rays for treatment of cancer, but more convenient gamma-ray sources produced in nuclear reactors now are more frequently chosen for medical therapy.

---

*See *Cryogenics, The Uncommon Cold,* another booklet in this series, for an explanation of this branch of science.

# EARLY HISTORY

## Attempts To Form Compounds

As in the case of other elements, the discovery of the noble gases was followed by an examination of their chemical properties. It soon became obvious that these elements were different—they would not enter into chemical combination with any other elements or with one another. Many attempts were made to induce chemical reactions between noble gases and both metals and nonmetals. A great many techniques were used but none proved successful. Although many claims were made that compounds had been formed containing noble gas atoms chemically bound to other atoms, most of these either were unconvincing or shown to be incorrect. The scientists who came closest to success were the American chemists, Don Yost and Albert Kaye. In 1933 they set out to test the prediction, made that year by another American, Linus Pauling, that krypton and xenon might react with fluorine. Yost and Kaye passed electric discharges through mixtures of xenon and fluorine and of krypton and fluorine. Their results were inconclusive and they stated in a communication to the *Journal of the American Chemical Society*, "It cannot be said that definite evidence for compound formation was found. It does not follow, of course, that xenon fluoride is incapable of existing".

Very soon after the discovery of the noble gases it was shown that argon, krypton, and xenon will form hydrates—compounds in which the gases are associated with water molecules. At first the hydrates were thought to be true chemical compounds, but they were later shown to be *clathrate* compounds; in this type of compound the inert gas is trapped in holes in a crystalline "cage" formed by the water molecules. The host molecule in hydrates is water, but several other clathrate hosts have also been used, such as the organic compounds phenol and quinol. For a compound to act as a host the cavities in its crystalline structure must be large enough to provide room for the inert gas atom, but small enough to keep it trapped in the cage. So far no host molecules have been found whose cages are small enough to keep helium or neon atoms trapped, so no

clathrate compounds of these gases are known. Incidentally, the phenomenon of clathrate formation provides a method of separating neon from argon by trapping the argon in a clathrate cage and pumping off the neon.

Clathrate compounds are not true chemical compounds, because they do not contain real chemical bonds. The only forces between the inert gas and the host molecule are relatively weak electrostatic interactions. The inert gas is readily released by destroying the crystalline cage, either by dissolving the host in a suitable solvent or by heating it to its melting point.

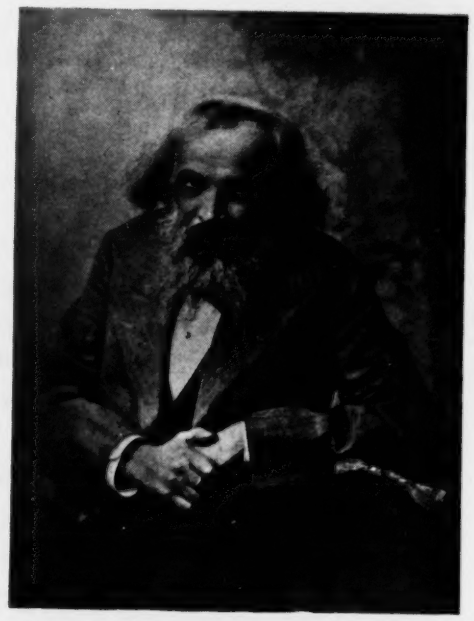
## Why the Gases Are Inert

Before discussing the reasons for the inertness of the noble gases it is interesting to look at the relationships between elements, and how they combine chemically with one another. The theory that each element has a fixed combining capacity was proposed by the English chemist Sir Edward Frankland in 1852. This capacity was called the *valence* of an atom. As most of the elements then known would combine with either oxygen or hydrogen, the valence values were related to the number of atoms of oxygen or hydrogen with which one atom of each element would combine. Two atoms of hydrogen combine with 1 atom of oxygen to form $H_2O$, so hydrogen was given a valence of 1, and oxygen a valence of 2. The valence of any other element was then the number of atoms of hydrogen (or twice the number of oxygen atoms) that combined with 1 atom of that element. In ammonia we have the formula $NH_3$, so nitrogen has a valence of 3; in carbon dioxide, $CO_2$, the carbon valence is 4. Valences are always whole numbers. Some elements exhibit more than one valence, and the maximum valence appears to be 8.

In the late 1860s the Russian chemist Dmitri Mendeleev made an intriguing observation when listing the elements in the order of increasing atomic weights. He found that the first element after hydrogen was lithium with a valence of 1, the second heaviest was beryllium with a valence of 2, the third, boron with a valence of 3, and so on. As he continued he found a sequence of valences that went 1, 2, 3, 4,

3, 2, 1, and then repeated itself. If he arranged the elements in vertical columns next to one another, in the order of increasing atomic weights, he found the elements in each horizontal row across the page had the same valence and strikingly similar chemical properties.

This kind of periodicity, or regular recurrence, had been noted by other scientists, but Mendeleev made a great step



*Dmitri Mendeleev*

forward by leaving gaps in his table where the next known element, in order of weight, did not fit because it had the wrong valence or the wrong properties. He predicted that these gaps would be filled by yet-to-be-discovered elements, and he even went as far as to predict the properties of some of these elements from the position they would occupy in his table. A reproduction of an early version of Mendeleev's Periodic Table of the Elements is shown in Figure 4. As can be seen, this was based on the 63 elements then known. In later versions of the Table the elements are arranged in order across the horizontal rows, and those with similar properties fall in the same vertical column.

At the time of the setting up of the Periodic Table the noble gases were still undiscovered. There were no gaps left for them, as spaces could be left only where at least 1 element in a group was already known. When argon was discovered some problem therefore arose as to its place

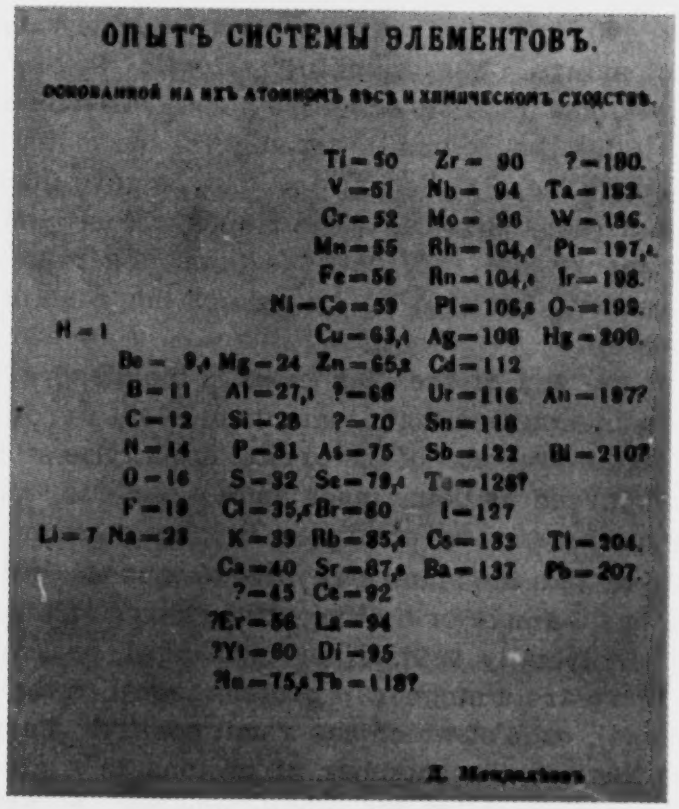

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.
ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.
Ti = 50 Zr = 90 ? = 180.
V = 51 Nb = 94 Ta = 182.
Cr = 52 Mo = 96 W = 186.
Mn = 55 Rh = 104,4 Pt = 197,4.
Fe = 56 Ru = 104,4 Ir = 198.
Ni = Co = 59 Pl = 106,6 O = 199.
H = 1 Cu = 63,4 Ag = 108 Hg = 200.
Be = 9,4 Mg = 24 Zn = 65,2 Cd = 112
B = 11 Al = 27,4 ? = 68 Ur = 116 Au = 197?
C = 12 Si = 28 ? = 70 Sn = 118
N = 14 P = 31 As = 75 Sb = 122 Bi = 210?
O = 16 S = 32 Se = 79,4 Te = 128?
F = 19 Cl = 35,5 Br = 80 I = 127
Li = 7 Na = 23 K = 39 Rb = 85,4 Cs = 133 Tl = 204.
Ca = 40 Sr = 87,6 Ba = 137 Pb = 207.
? = 45 Ce = 92
?Er = 56 La = 94
?Yt = 60 Di = 95
?In = 75,6 Th = 118?
Д. Менделѣевъ

**Figure 4** *Above is an early (1869) version of Mendeleev's Periodic Table. The heading reads, "Tentative system of the elements". The subheading reads, "Based on atomic weights and chemical similarities". This table is reproduced from* Dmitri Ivanovich Mendeleev, *N. A. Figurovskii, Russian Academy of Science, Moscow, 1961.*

in the periodic system. Its atomic weight suggested it might belong somewhere near potassium. When its lack of chemical reactivity was discovered, Mendeleev proposed that it had zero valence and should come between chlorine and potassium. He suggested that a group of such gases might be found. The valence periodicity then would be 0, 1, 2, 3, 4, 3, 2, 1. This new group led to a complete periodicity of 8, which we shall see is a very significant number.

Both Frankland and Mendeleev based their ideas on their knowledge of chemical properties. The theoretical support for both proposals came with the development of a theory of atomic structure and the *electronic* theory of valence. Theories stating that matter is composed of small, indivisible particles, called atoms, had been proposed as

early as 400 B.C., but were of a philosophic rather than scientific nature. The scientific atomic theory really started with the English scientist John Dalton in the 19th century. In his theory small, indivisible, and indestructible particles also were called atoms, but he gave them properties that had physical significance. More important, Dalton's theory not only would explain observed experimental results, but also could predict the results of new experiments.

Toward the end of the 19th century the discovery of the electron demonstrated that atoms themselves were divisible and led to the proposal of the orbital atom. The atom came to be considered as being made up of a nucleus, containing most of the mass, and electrons revolving around the nucleus rather like the planets revolve around the sun.* Each electron has a single or unit negative charge and the entire atom is electrically neutral, or uncharged, because in the nucleus there are a number of protons (equal to the number of electrons), each of which has a unit positive charge.

**Atomic Number** The number of protons in a given atom of an element is called the *atomic number*. In addition to the protons, the nucleus contains uncharged particles called neutrons. The neutrons and protons have about the same mass, and the electrons, by comparison, have negligible mass. An element of atomic mass (A) and atomic number (Z) will have a nucleus consisting of Z protons and (A−Z) neutrons, and this will be surrounded by Z electrons. For example, an atom of lithium with mass (A) of 7 and atomic number (Z) of 3 will have a nucleus consisting of 3 protons and 4 neutrons (A−Z), surrounded by 3 electrons.

The lightest element, hydrogen, has Z equal to 1, and each successively heavier element differs from the one preceding it by an increase of 1 in Z, and has one more proton and one more electron than the next lighter one. Thus, the second heaviest element, helium, has Z equal to 2, and so on. For the heavier elements, such as uranium (Z = 92), one might imagine a chaotic situation with many

*This theoretical "model" of the atom has since been modified to explain additional experimental results more fully. Now an atom often is considered as a nucleus with electrons moving rapidly and randomly around it, and having no definite boundary surface.

electrons buzzing all around the nucleus. Fortunately, the electrons are restricted to movement in certain fixed orbits or *shells.** The number of electrons in each shell, and the order in which additional electrons build up the shells of heavier elements, is governed by quantum mechanical considerations.† The first shell may contain 2 electrons, the second one 8, the third 18 and so on. However, the maximum number of electrons possible in any outermost shell is 8.

**Subshells** The shells themselves are actually split into subshells, which are designated by the letters *s*, *p*, *d*, and *f*, successively moving outward from the nucleus. The number of electrons in a given sublevel is restricted, being a maximum of 2 for *s*, 6 for *p*, 10 for *d*, and 14 for *f*. The various shells are distinguished from one another by numbers from 1 to 7, where 1 indicates the innermost shell and 7 the outermost. A further restriction is that there is only an *s* sublevel for the first shell, only *s* and *p* for the second, and only *s*, *p*, and *d* for the third. Beyond the third level *s*, *p*, *d*, and *f* sublevels are all permitted. These restrictions are actually the same as those indicated in the preceding paragraph; namely, the first shell contains 2 electrons, which we write $1s^2$, the second shell has 8, written $2s^2 2p^6$, the third 18, written $3s^2 3p^6 3d^{10}$.

The electrons do not necessarily fill the shells and subshells in consecutive order. The first (lightest) 18 elements' electrons are added regularly, the electrons filling the 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* subshells in sequence. However, in the nineteenth element, the new electron does not go into the 3*d* subshell, as might be expected, but into the 4*s* subshell. (Questions of this sort are decided on the basis of energy considerations. It is energetically more favorable to put the 19th electron into the 4*s* subshell.) From this point on we can write down the electronic configurations of the succeeding (heavier) elements only if we know the

---

*A shell is also referred to in other theories as an *energy level.*

†Quantum mechanics is a form of mathematical analysis involving quanta, or definite units of energy in which radiation is emitted or absorbed. The different orbits, or energy levels, of planetary electrons are separated from each other by whole numbers of quanta.

order in which the subshells are filled. We should note that when the electrons do go into the 3*d* subshell this is considered to be inside the 4*s* level. Consequently, there can be 10 electrons in this subshell without violating the rule of having a maximum of 8 electrons in the outermost shell.

Table II
ELECTRONIC STRUCTURES OF SELECTED ELEMENTS

| Element | Atomic Number | Electronic Structure |
|---|---|---|
| Hydrogen | 1 | $1s^1$ |
| Helium | 2 | $1s^2$ |
| Lithium | 3 | $1s^2, 2s^1$ |
| Beryllium | 4 | $1s^2, 2s^2$ |
| Boron | 5 | $1s^2, 2s^2, 2p^1$ |
| Neon | 10 | $1s^2, 2s^2, 2p^6$ |
| Sodium | 11 | $1s^2, 2s^2, 2p^6, 3s^1$ |
| Argon | 18 | $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ |
| Potassium | 19 | $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ |
| Calcium | 20 | $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ |
| Scandium | 21 | $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1, 4s^2$ |
| Titanium | 22 | $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$ |

This is always the case for *d* and *f* subshells: they are always inside the next or next-but-one *s* subshell when being filled. Table II gives the electronic structures for several elements.*

Now we are ready to look at the electronic theory of valence and some of its consequences. About 1920 a number of chemists, most notably the American G. N. Lewis, suggested that the electrons in the outermost shells were responsible for elements' chemical reactions. Compounds (that is, molecules) are formed by the transfer or sharing of electrons, and the number of such electrons provided or obtained by an atom of any element during the combining process is its valence. However, there is a kind of regulation of the number of electrons that can participate in this bonding. It was suggested that the elements were always being prodded to attain the maximum number of electrons in their outer shell, namely 8. An electronic structure with

*For a discussion of the electronic configuration of another interesting family of the elements see *Rare Earths, The Fraternal Fifteen,* a companion booklet in this series.

8 electrons in the outer shell is considered to be more stable and is called a *closed-shell* arrangement. Atoms, then, tend to adjust their electronic structure to that of the *nearest* element with a completed outer shell. The adjustment is made by losing, gaining, or sharing electrons with other atoms.

The closed-shell arrangement of electrons happens to be the electronic structure of atoms of the noble gases. Moreover, *only* the 6 noble gases have this arrangement of maximum stability. This fact is the basis for the shorthand notation for writing electronic structures. From Table II we can see the electronic structure of sodium is $1s^2$, $2s^2$, $2p^6$, $3s^1$; sodium has 1 electron more than the closed-shell arrangement $1s^2$, $2s^2$, $2p^6$, which is the electronic structure of neon. The sodium electronic configuration can therefore be written (Ne), $3s^1$. Similarly potassium can be written (Ar), $4s^1$, scandium can be indicated by (Ar), $3d^1$, $4s^2$, etc. The closed-shell arrangements are also called *cores*.

Two atoms with the same number of electrons outside a stable core would tend strongly to adjust their electronic configuration in a similar manner; that is, they would have the same valence and therefore the same chemical properties. This fact is borne out by the fact that elements in the same group in the Periodic Table have the same outer electronic structures. Table III on pages 24–25 is a modern version of the Periodic Table, showing the electronic structures. Note that different elements sometimes appear to have identical electronic structures; for example, the outer shells of calcium and zinc are both $4s^2$. However, calcium is (Ar), $4s^2$ while zinc is (Ar), $3d^{10}$, $4s^2$. The presence of the complete $d$ subshell causes zinc to have somewhat different properties. Those elements in which the $d$ and $f$ subshells are being filled are called *transition* elements, as opposed to the *nontransition* elements in which the electrons are going into $s$ and $p$ subshells.

The fact that the noble gases have completed outer shells means that they have nothing to gain by losing, gaining, or sharing electrons. They already have the stable electronic structures that other elements are striving to attain. This means that they should have *zero* valence and

should not form chemical compounds. Thus, the observed experimental fact that the gases were inert was supported by theory. This startling agreement between experiment and theory was successful in discouraging attempts to make chemical compounds with the noble gases for a period of almost 40 years.

## PREPARATION OF THE FIRST XENON COMPOUNDS

Until 1962 all the accepted evidence pointed to the fact that the noble gases were chemically inert. A few brave souls had predicted that compounds of them might exist, but textbooks and teachers stressed the inertness of the gases and these statements went unchallenged.

As we have seen, the discovery of the first noble gas was an outcome of an investigation of the density of nitrogen. The discovery of the first chemical compound of a noble gas was also a by-product of an unrelated investigation. The beginning really goes back to the Manhattan Project* and the production of the first atomic bomb. An important ingredient for the bomb was the uranium isotope $^{235}U$. This was separated from natural uranium (which is a mixture containing mostly another isotope, $^{238}U$) by gaseous diffusion, the "gas" for this process being a volatile uranium compound, uranium hexafluoride, $UF_6$. This wartime interest in $UF_6$ created an interest in other metallic hexafluorides, compounds containing 6 fluorine atoms bound to 1 metal atom. The study of the properties of these compounds, and the search for new hexafluorides, was undertaken after the war in many laboratories, especially those of the U. S. Atomic Energy Commission, which had workers experienced in handling such chemically reactive materials. A group of scientists at the AEC's Argonne National Laboratory was particularly active in this field. They discovered hexafluorides of platinum, technetium, ruthenium, and rhodium, and investigated the properties of these and other hexafluoride molecules.

---

*The World War II code name for the program of the War Department unit that predated the present Atomic Energy Commission.

The next step in the story took place at the University of British Columbia in Vancouver, where Neil Bartlett, a young British chemist, was doing research on fluorides of platinum. He and one of his colleagues discovered a compound containing platinum, oxygen, and fluorine, which they formulated as $O_2^+PtF_6^-$. In order to form this type of compound, an electron must be removed from the $O_2$ part of the molecule, leaving it with a net positive charge. This electron becomes associated with the $PtF_6$ part, giving this part a net negative charge. The surprising thing about this reaction is that the energy required to remove an electron from an oxygen molecule, the *ionization potential,* is quite high. As a matter of fact, no compound containing $O_2^+$ had ever been known before the discovery of $O_2^+PtF_6^-$. Although the $O_2^+PtF_6^-$ they first synthesized was not made directly from $PtF_6$, Bartlett soon found that $PtF_6$ and molecular oxygen will react to give this compound. This suggested to him that $PtF_6$ (platinum hexafluoride) must have a strong affinity for electrons.

Soon after the discovery of $O_2^+PtF_6^-$. Bartlett realized that the ionization potential of xenon is almost exactly the same as that of molecular oxygen. This led him to wonder if the platinum hexafluoride, with its powerful electron-attracting properties, could pull an electron away from xenon to form a chemical compound. He decided to try an experiment to confirm this idea. He filled a glass container with a known amount of the deep red platinum hexafluoride vapor and separated it by a glass diaphragm from a similar container filled with a known amount of the colorless xenon gas. When the diaphragm between them was broken there was an immediate and spectacular reaction: The 2 gases combined to produce a yellow solid! Initial measurements of the amounts of gases reacting indicated that the combining ratio was 1-to-1. In the June 1962 *Proceedings of the Chemical Society of London,* Bartlett reported preparation of the world's first compound in which a noble gas was chemically bound — the yellow solid, $Xe^+PtF_6^-$.

The announcement was greeted with surprise and in some places disbelief. This is not surprising since one of the accepted and revered dogmas of chemistry had just

been shattered by his one experiment. More surprises were yet to come.

The scientists at Argonne, where $PtF_6$ had been first made, confirmed Bartlett's results almost as soon as they learned of his experiments. They went on to extend his work, and showed that xenon would also combine — amazingly — with the hexafluorides of plutonium, ruthenium, and rhodium.

However, things were not as straightforward as they had at first seemed. The combining ratios, which had been 1-to-1 in the first experiments, were found to vary irregularly from one hexafluoride to another, and sometimes even varied for the same hexafluoride. Even with $PtF_6$ it appeared that there might be at least 2 compounds formed, $XePtF_6$ and $Xe(PtF_6)_2$. This threw some doubt on the idea that $XePtF_6$ and $O_2^+PtF_6^-$ might be completely analogous. The group at Argonne began to wonder if the attraction between xenon and the hexafluorides was due, not to the strong attraction of the hexafluorides for electrons, but instead to the hexafluorides' ability to provide fluorine, that is, to act as *fluorinating* agents. If this were so, it was reasoned, the xenon might actually react with fluorine itself.

Howard H. Claassen, then an Argonne consultant from Wheaton College, and Henry Selig and John G. Malm of the Argonne Chemistry Division next decided to test this idea. A known amount of xenon was condensed in a nickel container and a fivefold excess of fluorine was added. The container was sealed and heated to 400 °C for 1 hour. After cooling the container to the temperature of dry ice (–78 °C), the experimenters pumped the unreacted gas away. If xenon were really an inert gas, the container should have been empty at this stage. To everyone's surprise it was *not* empty when weighed. Furthermore, the gain in weight could be accounted for exactly by assuming that all the xenon initially present had reacted with fluorine to form a compound with the formula $XeF_4$. The contents of the can was sublimed into a glass tube as brilliant, colorless crystals (Figure 5). Within weeks of the time the original announcement of the preparation of $XePtF_6$ reached Argonne, a simple compound containing a noble gas and one

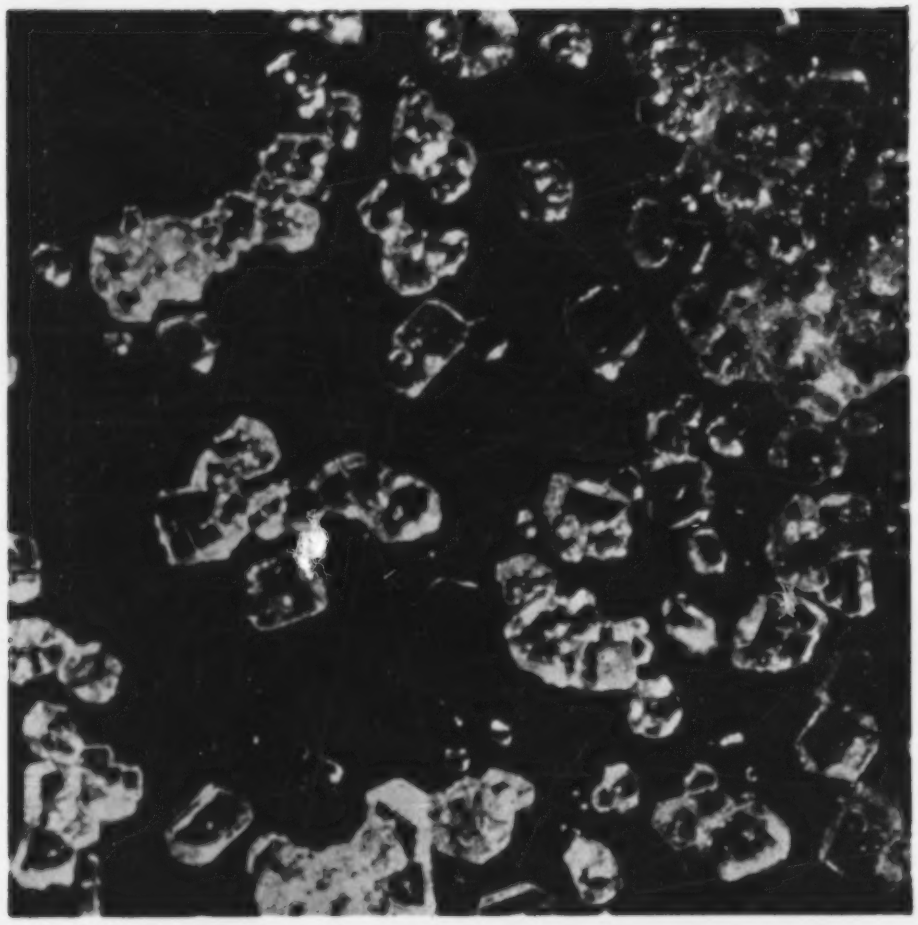


**Figure 5** *Crystals of xenon tetrafluoride. (Also see cover photograph.)*

other element had been prepared. The date was August 2, 1962.

One might wonder why the expression "more surprises were yet to come" was used a couple of paragraphs ago. Those who had objected to the "violation" of the idea of absolute inertness of the noble gases could still rationalize that a compound as exotic as one between Xe and $PtF_6$ might not contain true chemical bonding, and that it might even be a new type of clathrate compound. The preparation of $XeF_4$ removed all such possible explanations, and the chemical world was faced with the naked truth that at least one "inert" gas was not inert. Chemical textbooks became obsolete overnight in this respect, and professors and teachers had to rewrite their lecture notes.

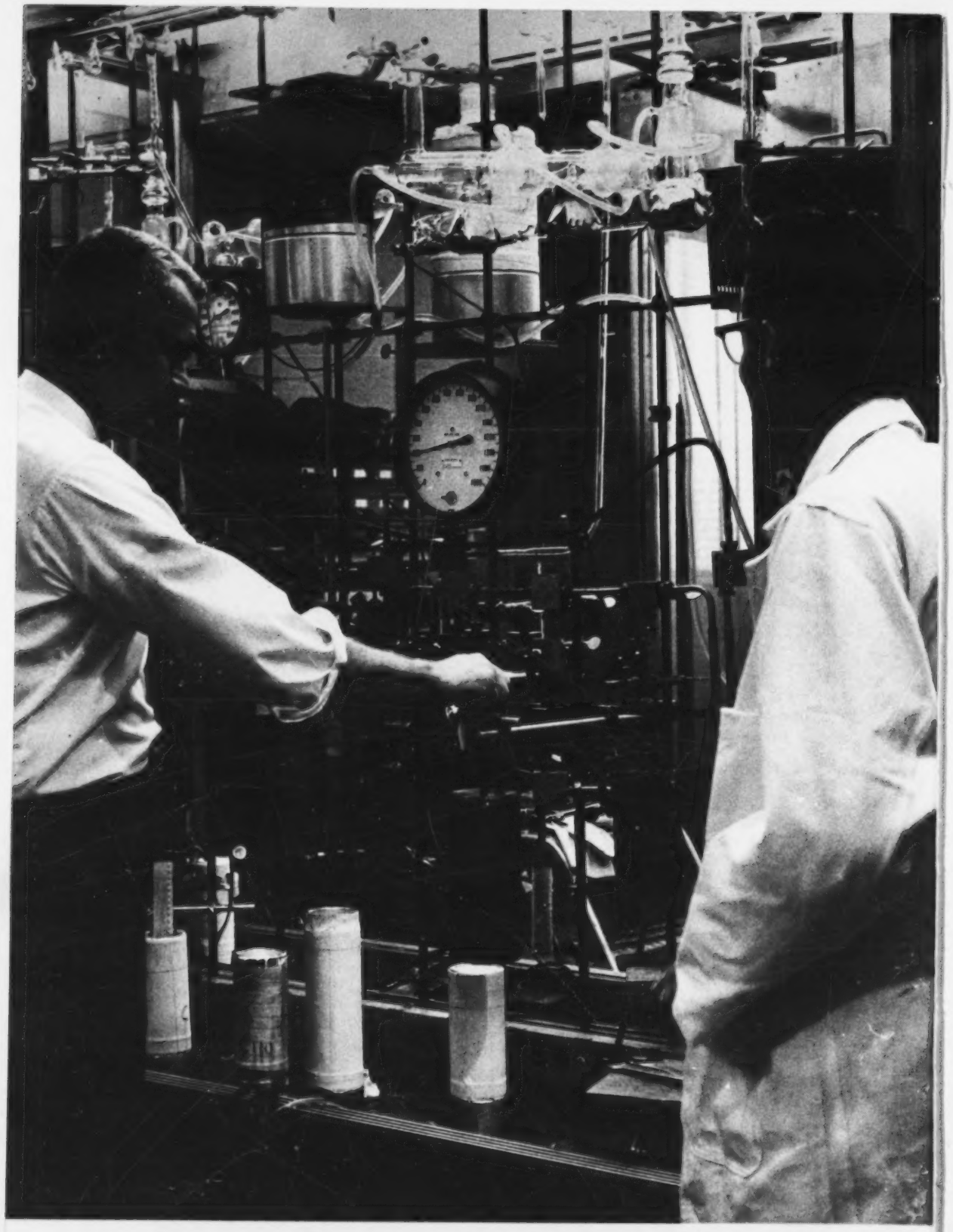


**Figure 6** *John G. Malm (left) and Howard H. Claassen adjusting apparatus similar to that used for the first preparation of $XeF_4$ at Argonne National Laboratory.*

## COMPOUNDS OF XENON

### Fluorine-Containing Compounds

As we have already seen, the first noble gas compounds contained the element fluorine.* Of the many compounds discovered since then, it turns out that they all either contain fluorine or are made from fluorine-containing compounds. Let us consider first the 3 known binary fluorides, that is, compounds containing only xenon and fluorine. By heating together a mixture of xenon and fluorine under appropriate conditions, chemists can produce xenon difluoride, $XeF_2$, xenon tetrafluoride, $XeF_4$, and xenon hexafluoride, $XeF_6$. Which of these fluorides is produced depends on the ratio of fluorine to xenon, the temperature of the reaction, and the pressure in the reaction vessel. These may be adjusted to form any one of the 3 fluorides in a reasonably pure state. If care is not taken, however, mixtures of the fluorides result and these are difficult to separate. Table IV on page 26 shows the conditions that have been used to prepare several-gram quantities of $XeF_2$, $XeF_4$, and $XeF_6$.

In order to prepare a fluoride of xenon it is only necessary to have a source of fluorine atoms, which then react with the xenon. Heating fluorine gas is one way to produce such atoms; they have also been produced by subjecting fluorine, or fluorine-containing compounds, to electric discharges or ionizing radiations, such as the gamma rays from a cobalt-60 source or a beam of electrons, a beam of ultraviolet light, or a beam of neutrons from a reactor.

The fact that xenon fluorides can be formed answered a puzzling question that had been plaguing scientists and engineers who were studying reactor fuels.† In experiments to test the fuels and fuel assemblies for a molten-salt reactor, a mixture of lithium fluoride, beryllium fluoride, zirconium fluoride, and uranium fluoride was

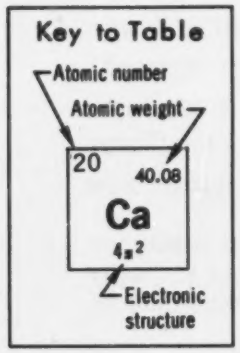
*Fluorine is the most active nonmetallic element, and combines with all other elements (disregarding the noble gases) so strongly that it cannot be prepared from any of its natural compounds by any purely chemical reduction.

†For more about reactors, see *Nuclear Reactors* and *Atomic Fuel*, companion booklets in this series.

# Table III PERIODIC TABLE OF THE ELEMENTS

| PERIOD \ GROUP | Ia | IIa | IIIa | IVa | Va | VIa | VIIa | VII | Ib | IIb | IIIb | IVb | Vb | VIb | VIIb | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 1.00797 H $1s$ | | | | | | | | | | | | | | | 2 4.0026 He $1s^2$ |
| 2 | 3 6.939 Li $2s$ | 4 9.0122 Be $2s^2$ | | | | | | | | | 5 10.811 B $2s^22p^1$ | 6 12.0111 C $2s^22p^2$ | 7 14.0067 N $2s^22p^3$ | 8 15.9994 O $2s^22p^4$ | 9 18.9984 F $2s^22p^5$ | 10 20.183 Ne $2s^22p^6$ |
| 3 | 11 22.9898 Na $3s$ | 12 24.312 Mg $3s^2$ | | | | | | | | | 13 26.9815 Al $3s^23p^1$ | 14 28.086 Si $3s^23p^2$ | 15 30.9738 P $3s^23p^3$ | 16 32.064 S $3s^23p^4$ | 17 35.453 Cl $3s^23p^5$ | 18 39.948 Ar $3s^23p^6$ |
| 4 | 19 39.102 K $4s$ | 20 40.08 Ca $4s^2$ | 21 44.956 Sc $3d^14s^2$ | 22 47.90 Ti $3d^24s^2$ | 23 50.942 V $3d^34s^2$ | 24 51.996 Cr $3d^54s^1$ | 25 54.938 Mn $3d^54s^2$ | 26 55.847 Fe $3d^64s^2$ | 27 58.933 Co $3d^74s^2$ | 28 58.71 Ni $3d^84s^2$ | 29 63.54 Cu $3d^{10}4s^1$ | 30 65.37 Zn $3d^{10}4s^2$ | 31 69.72 Ga $4s^24p^1$ | 32 72.59 Ge $4s^24p^2$ | 33 74.922 As $4s^24p^3$ | 34 78.96 Se $4s^24p^4$ | 35 79.909 Br $4s^24p^5$ | 36 83.80 Kr $4s^24p^6$ |
| 5 | 37 85.47 Rb $5s$ | 38 87.62 Sr $5s^2$ | 39 88.905 Y $4d^15s^2$ | 40 91.22 Zr $4d^25s^2$ | 41 92.906 Nb $4d^45s^1$ | 42 95.94 Mo $4d^55s^1$ | 43 (99) Tc $4d^55s^2$ | 44 101.07 Ru $4d^75s^1$ | 45 102.905 Rh $4d^85s^1$ | 46 106.4 Pd $4d^{10}$ | 47 107.870 Ag $4d^{10}5s^1$ | 48 112.40 Cd $4d^{10}5s^2$ | 49 114.82 In $5s^25p^1$ | 50 118.69 Sn $5s^25p^2$ | 51 121.75 Sb $5s^25p^3$ | 52 127.60 Te $5s^25p^4$ | 53 126.904 I $5s^25p^5$ | 54 131.30 Xe $5s^25p^6$ |
| 6 | 55 132.905 Cs $6s$ | 56 137.34 Ba $6s^2$ | 57 138.91 La* $5d^16s^2$ | 72 178.49 Hf $5d^26s^2$ | 73 180.948 Ta $5d^36s^2$ | 74 183.85 W $5d^46s^2$ | 75 186.2 Re $5d^56s^2$ | 76 190.2 Os $5d^66s^2$ | 77 192.2 Ir $5d^96s^0$ | 78 195.09 Pt $5d^96s^1$ | 79 196.967 Au $5d^{10}6s^1$ | 80 200.59 Hg $5d^{10}6s^2$ | 81 204.37 Tl $5d^{10}6s^26p^1$ | 82 207.19 Pb $6s^26p^2$ | 83 208.980 Bi $6s^26p^3$ | 84 (210) Po $6s^26p^4$ | 85 (210) At $6s^26p^5$ | 86 (222) Rn $6s^26p^6$ |
| 7 | 87 (223) Fr $6s^26p^67s^1$ | 88 (226) Ra $6s^26p^67s^2$ | 89 (227) Ac** $6s^26p^66d^17s^2$ | | | | | | | | | | | | | |

**Key to Table**




| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Lanthanides | 58 140.12 Ce $4f^26s^2$ | 59 140.907 Pr $4f^36s^2$ | 60 144.24 Nd $4f^46s^2$ | 61 (147) Pm $4f^56s^2$ | 62 150.35 Sm $4f^66s^2$ | 63 151.96 Eu $4f^76s^2$ | 64 157.25 Gd $4f^75d^16s^2$ | 65 158.924 Tb $4f^96s^2$ | 66 162.50 Dy $4f^{10}6s^2$ | 67 164.930 Ho $4f^{11}6s^2$ | 68 167.26 Er $4f^{12}6s^2$ | 69 168.934 Tm $4f^{13}6s^2$ | 70 173.04 Yb $4f^{14}6s^2$ | 71 174.97 Lu $4f^{14}5d^16s^2$ |
| **Actinides | 90 232.038 Th $6d^27s^2$ | 91 (231) Pa $5f^26d^17s^2$ | 92 238.04 U $5f^36d^17s^2$ | 93 (237) Np $5f^46d^17s^2$ | 94 (242) Pu $5f^67s^2$ | 95 (243) Am $5f^77s^2$ | 96 (247) Cm $5f^76d^17s^2$ | 97 (247) Bk $5f^76d^27s^2$ | 98 (251) Cf $5f^96d^17s^2$ | 99 (254) Es $5f^{11}6s^26d^67s^2$ | 100 (253) Fm $5f^{12}6s^26p^67s^2$ | 101 (256) Md $5f^{13}6s^26p^67s^2$ | 102 (254) No | 103 (257) Lw |

Table IV
CONDITIONS USED FOR PREPARING THE XENON FLUORIDES

| Compound | Ratio $Xe/F_2$ | Temperature (°C) | Time (hours) | Pressure (atmospheres) |
|---|---|---|---|---|
| $XeF_2$ | 7.5 : 1 | 400 | 16 | 75 |
| $XeF_4$ | 1 : 5 | 400 | 1 | 6 |
| $XeF_6$ | 1 : 20 | 250 | 16 | 50 |

used as the fuel. This was sealed in a container and subjected to neutron irradiation. Under these conditions the $^{235}U$ in the uranium fluoride, $UF_4$, undergoes fission. The fission results in the $^{235}U$ atoms' breaking up into new fission-product atoms of nearly equal mass, and some free neutrons, and the release of a large amount of energy. Among the expected fission products there always are some xenon isotopes, and the amount of xenon so produced is sometimes used as a measure of the amount of fission that has taken place. You can imagine the surprise of the scientists when no xenon could be found in the gases from the molten-salt reactor experiments, although other products showed that fission had undoubtedly taken place.

**Puzzle Explained** With the discovery of xenon tetrafluoride the puzzle was explained. It turned out that free fluorine is generated in the reactor-fuel mixture by the neutron irradiation. Under certain conditions this fluorine can react with the fission product xenon to form a xenon fluoride. In those cases where no xenon was found, the conditions had been right for xenon fluoride formation. This was another case in which a discovery in one field of science answered a problem in another.

Perhaps the most startling experiment with xenon and fluorine was reported towards the end of 1965. Xenon and fluorine when mixed in a dry glass flask will react if the mixture is exposed to sunlight! In this case the energy provided by the sunlight is enough to produce the needed fluorine atoms. This being the case, one may wonder why it took so many years to prepare the first noble gas compounds. Several explanations have been offered, such as the difficulty in getting thoroughly dried glassware, and lack of knowledge of the techniques for handling fluorine

Table V
PHYSICAL PROPERTIES OF THE XENON FLUORIDES

| Compound | Color of Solid | Color of Vapor | Melting Point (°C) | Vapor Pressure at 25°C (mm) | Density gm/cc at 25°C |
|---|---|---|---|---|---|
| $XeF_2$ | Colorless | Colorless | 129 | 4.6 | 4.32 |
| $XeF_4$ | Colorless | Colorless | 117 | 2.5 | 4.04 |
| $XeF_6$ | Colorless | Greenish-Yellow | 49.5 | 27 | 3.41 |

and reactive fluorides. These undoubtedly played a part, but the major factor was probably the lack of an adequate amount of xenon. (Until recently xenon was not generally available in most laboratories because of its high cost.)

The xenon fluorides are colorless crystalline materials at room temperature, but they react readily with moisture. For this reason they must be handled in thoroughly dried equipment and are usually manipulated in metal vacuum systems. A typical experimental setup is shown on page 22. The necessity of avoiding a reaction with water (hydrolysis) is extremely important, as we shall see later. Providing this precaution is observed, the fluorides are stable at room temperature and can be stored for prolonged periods in nickel containers.

Some of the physical properties of the fluorides are given in Table V. Each of the fluorides will react with hydrogen, forming hydrogen fluoride and liberating elemental xenon; for example,

$$XeF_4 + 2H_2 \rightarrow Xe + 4HF$$

The relative ease of this reaction with hydrogen establishes $XeF_6$ as the most reactive of the xenon fluorides, and $XeF_2$ as the least reactive. This order of reactivity has been confirmed by other experiments, in which the xenon fluorides act as fluorinating agents. In addition, it has been found that both $XeF_2$ and $XeF_4$ can be stored in thoroughly dried glass containers, but $XeF_6$ reacts even with dry glass or quartz. Note that xenon, in forming the three fluorides, exhibits valences of 2, 4, and 6.

## Oxygen-Containing Compounds

Under normal conditions it does not appear to be possible to obtain a chemical reaction between oxygen and xenon or between oxygen and a xenon fluoride. In those cases where oxygen has been introduced into a xenon-containing compound the introduction has been achieved by the replacement of fluorine. One of the first oxygen-containing compounds to be discovered was xenon oxide tetrafluoride, $XeOF_4$. Chemists attempting to store $XeF_6$ in glass found that a clear, colorless liquid was formed by reaction of the $XeF_6$ with the glass. The liquid was analyzed and found to have the formula $XeOF_4$. The oxygen had been obtained from the glass, which may be regarded as silicon dioxide, $SiO_2$. The reactive fluorine in the $XeF_6$ replaced the oxygen in the $SiO_2$, converting it to $SiF_4$:

$$2XeF_6 + SiO_2 = 2XeOF_4 + SiF_4$$

Since fluorine has a valence of 1 and oxygen a valence of 2, 2 fluorine atoms had to be removed to allow the insertion of 1 oxygen atom.

This oxygen-containing compound is also formed when $XeF_6$ reacts with just enough water to provide for the replacement of 2 of the fluorine atoms. This reaction may be written:

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

Xenon oxide tetrafluoride is somewhat less reactive than $XeF_6$, but is more reactive than $XeF_4$. It may be kept unchanged in dried nickel containers, but it slowly attacks glass or quartz.

The reaction of $XeF_6$ with enough water to provide for the replacement of all 6 fluorine atoms with oxygen atoms yields $XeO_3$, xenon trioxide:

$$XeF_6 + 3H_2O = XeO_3 + 6HF$$

Xenon trioxide also results when $XeOF_4$ is allowed to remain in contact with glass for prolonged periods, or when

$XeOF_4$ reacts with water. The reaction of $XeF_4$ with water can also result in the formation of $XeO_3$. This is a somewhat surprising reaction, however. In $XeO_3$ the xenon has a valence of 6, the xenon being combined with three oxygen atoms each of valence 2. When $XeO_3$ is formed from $XeF_6$ or $XeOF_4$ the valence of the xenon in the original compounds is also 6. However, when $XeO_3$ is prepared from $XeF_4$, the valence of the xenon in the starting material is only 4. This type of reaction comes about by *disproportionation* of the xenon atoms; some of them end up in a higher valence state and some in a lower one, that is, some of the xenon atoms are oxidized and others are reduced. The production of xenon trioxide from xenon tetrafluoride and water may be formulated thus:

$$3XeF_4 + 6H_2O = Xe + 2XeO_3 + 12HF$$

Starting off with 3 xenon atoms each having a valence of 4, the procedure ends up with 1 xenon atom of valence zero and 2 of valence 6, thus balancing the valences. In alkaline solutions, for example caustic soda, the disproportionation can go a step further and yield compounds containing xenon with a valence of 8, such as sodium perxenate, $Na_4XeO_6$. The perxenate salts react with concentrated sulphuric acid to yield the 8-valent xenon tetroxide, $XeO_4$.

EXTREME CARE MUST BE TAKEN WITH BOTH OF THE XENON OXIDES, BECAUSE THEY ARE POWERFUL EXPLOSIVES UNDER CERTAIN CONDITIONS. Xenon trioxide is relatively safe in solution in water. When the water evaporates, however, the pure xenon trioxide is left in the form of colorless crystals, which are as powerful as TNT in their explosive power! Unlike the case with TNT, it is not known under what conditions the crystals can be handled safely, nor exactly what causes them to explode. This makes working with xenon trioxide *extremely hazardous.* Moreover, because the xenon fluorides react with moisture to give xenon trioxide, even working with *these* compounds can also be dangerous. The metal container shown in Figure 7 was damaged by the explosion of about 100 mg. (0.0035 oz.) of xenon trioxide. Even experienced and careful scientists have been injured when working with xenon

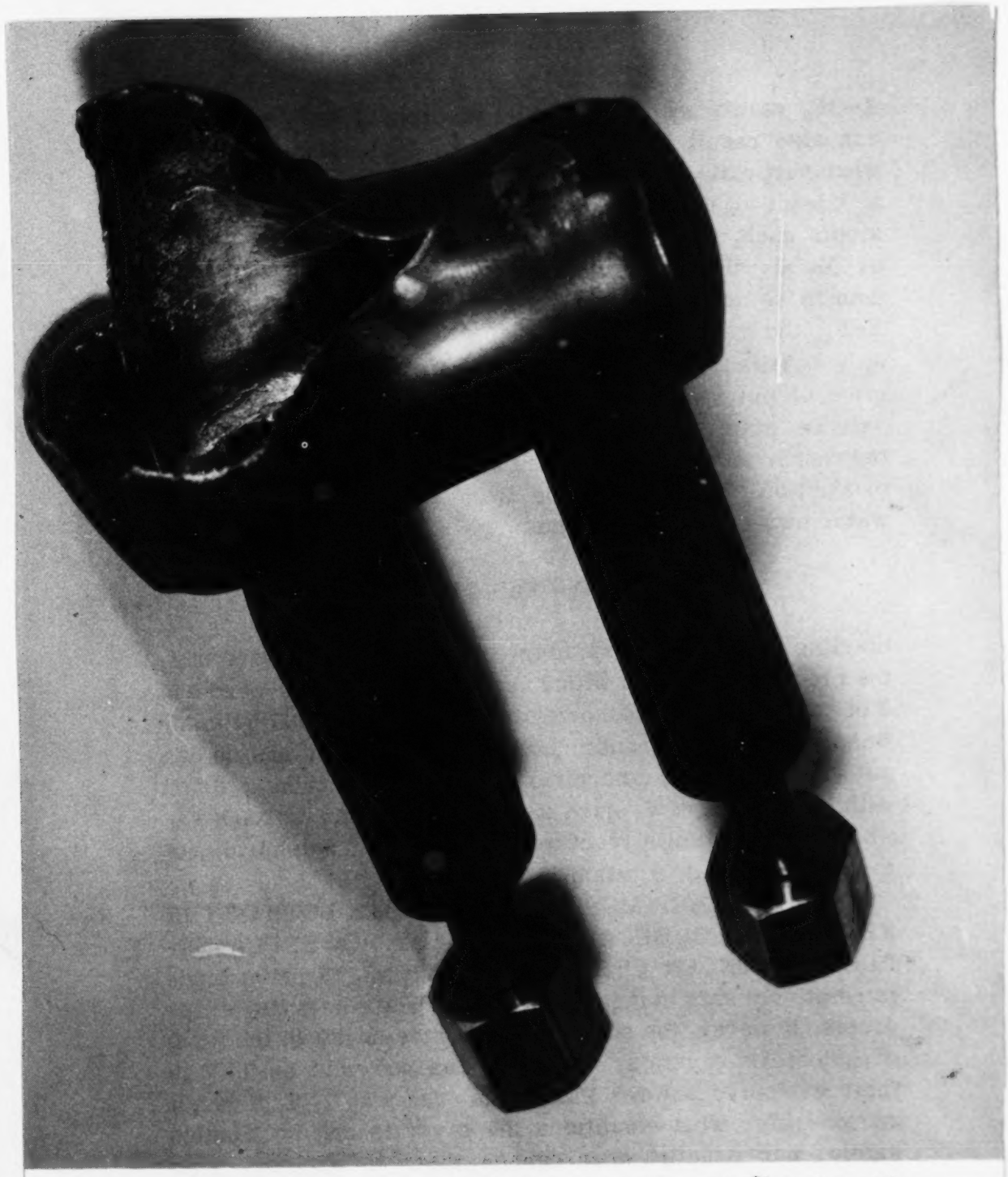


**Figure 7** *This nickel can, about 4 inches long and 1¾ inches wide (photo is approximately actual size), was ruptured by detonation of 100 milligrams of $XeO_3$.*

compounds. These, then, are not materials to be worked with in a basement laboratory in a home, but should only be handled in well-equipped laboratories by experienced workers who give every regard to safety precautions.

## More Complex Compounds

Mention has been made of $XePtF_6$ and similar compounds in which xenon combines with metal hexafluorides. The exact nature of these compounds is hard to elucidate and is still being investigated. Both xenon difluoride and xenon hexafluoride will react with a number of other fluorides to form *addition compounds*. Table VI shows the formulas of some of the complexes that have been reported. Apart

Table VI
COMPLEXES OF XENON AND KRYPTON FLUORIDES

| Noble Gas Compound | $XeF_2$ | $XeF_4$ | $XeF_6$ | $XeOF_4$ | $KrF_2$ |
|---|---|---|---|---|---|
| Complexing Fluoride | Ratio of Noble Gas Compound to Complexing Fluoride | | | | |
| NaF | * | * | 1:2 | * | * |
| KF | * | * | 1:2 | 1:3 | * |
| | | | | 1:6 | |
| RbF | † | † | 1:2 | 2:3 | † |
| | | | 1:1 | | |
| CsF | † | † | 1:2 | 1:3 | † |
| | | | 1:1 | 2:3 | |
| | | | | 1:1 | |
| $SbF_5$ | 1:2 | ‡ | 1:2 | 1:2 | 1:2 |
| | | | 1:1 | † | |
| | | | 2:1 | † | |
| $AsF_5$ | * | † | 1:1 | 2.1§ | ‡ |
| $BF_3$ | * | † | 1:1 | * | † |
| $TaF_5$ | 1:2 | † | † | † | † |
| $VF_5$ | * | * | 2:1 | ‡ | † |

*No compound formed.
†Has not been tried.
‡Compound forms; formula not yet known.
§Unstable above −20°C.

from their chemical composition, and a few physical properties, not much else is known about these complexes. Xenon tetrafluoride does not appear to form a similar series of addition compounds.

## COMPOUNDS OF OTHER NOBLE GASES

### Radon

The ionization potential of radon is the lowest of any of the noble gases, which might lead one to think it would be the most willing to form compounds. This may in fact be the case, but experiments with radon are severely hampered because of its high radioactivity. Work done with very small amounts of material (about one billionth of a gram) has shown that radon gas reacts with fluorine at 400°C to yield a compound that is not gaseous at room temperature, as both radon and fluorine are. The course of the reaction was followed only by monitoring with radiation detecting instruments the movement of the radioactivity associated with one of the products of decay of the radon. The formula of the compound produced has not been determined, and further investigation will be needed in which larger quantities of radon can be used. This will require elaborate shielding to protect the experimenters from the high radioactivity.

### Krypton

After xenon and radon, krypton should be the most likely of the remaining noble gases to form compounds. Its ionization potential is somewhat higher than that of either oxygen or xenon, and it will not react with platinum, ruthenium, or rhodium hexafluorides ($PtF_6$, $RuF_6$, and $RhF_6$, respectively). The simple heating of krypton and fluorine also has failed to produce a compound. However, a krypton fluoride compound can be formed under the more drastic experimental conditions of passing an electric discharge or an electron beam through a mixture of the 2 gases. The krypton fluoride will decompose almost as fast as it is formed if it is left in the discharge or beam zones. But if the container is immersed in a cold bath the krypton fluoride condenses on the container wall, and is thus removed from the zone in which the energy is generated. In this way krypton difluoride also has been produced, and possibly krypton tetrafluoride. The evidence for the formation of the latter is somewhat inconclusive, however.

Krypton difluoride is a colorless, crystalline compound that decomposes into krypton and fluorine at room temperature. At the temperature of dry ice, −78°C, krypton difluoride may be stored unchanged for prolonged periods of time. Chemically, it is a much more reactive compound than xenon difluoride, and in fact, its fluorinating properties appear to be even greater than those of xenon hexafluoride.

### Helium, Neon, and Argon

All evidence now available points to the fact that these gases are still inert. If one were to look at the properties of the fluorides of krypton we have just discussed, in comparison with those of the xenon fluorides, one would immediately expect that fluorides of the three lightest noble gases could be prepared only under extreme conditions, and even then would be stable at only low temperatures. Attempts to prepare compounds have so far failed, but who knows what may be found some day? Only a few years ago the idea of a xenon fluoride seemed preposterous, too.

## SHAPES OF MOLECULES

### Solid State

In solids, the molecules are condensed to form crystals, and the way in which the atoms are arrayed in the molecules may be determined by using beams of X rays or neutrons. When such a beam is directed at a crystal it either passes through the spaces between atoms undisturbed, or else it strikes an atom and is scattered or deflected. The amount of scattering can be detected and measured, giving a pattern that can be related to the location of the atoms and therefore to the structure of the crystal.

The determination of the actual array of the atoms in any unknown crystal has to be made in an indirect manner. A guess is made of its probable structure and the pattern that this structure would produce is calculated. This pattern is compared with the experimental pattern. When an exact match is obtained, it is apparent the structure is known. This used to be a long, tedious operation, but modern computer technology has simplified the process.

The atoms of material are spread out in all three dimensions throughout every crystal and this complexity in theory could lead to very complicated structures. Fortunately, it turns out that there are certain arrays of atoms

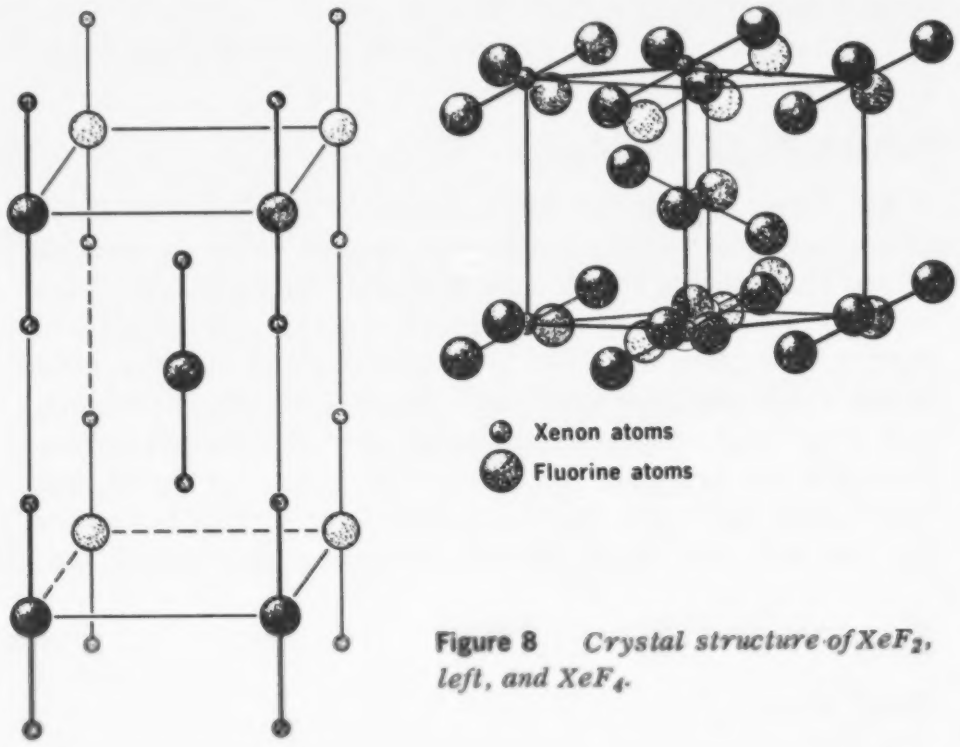



**Figure 8** *Crystal structure of $XeF_2$, left, and $XeF_4$.*

that repeat themselves throughout the crystal lattice; these are called "unit cells", and the problem is reduced to one of finding the locations of the atoms in each of the unit cells.

Both X-ray-diffraction and neutron-diffraction techniques have been used to determine the structures of $XeF_2$ and $XeF_4$, and the X-ray method alone has been used for $XeO_3$. Figure 8 shows the crystal structures of $XeF_2$ and $XeF_4$ so determined. The high reactivities of $XeF_6$, $XeOF_4$, and $KrF_2$ produce problems when an attempt is made to examine their solid phase structures. Samples to be examined by X-ray techniques are usually loaded into long, thin glass capillaries. Figure 9 shows a scientist positioning one such capillary in an X-ray camera. As $XeF_6$, $XeOF_4$, and $KrF_2$ are incompatible with glass, and also are most easily handled below room temperature, they require special

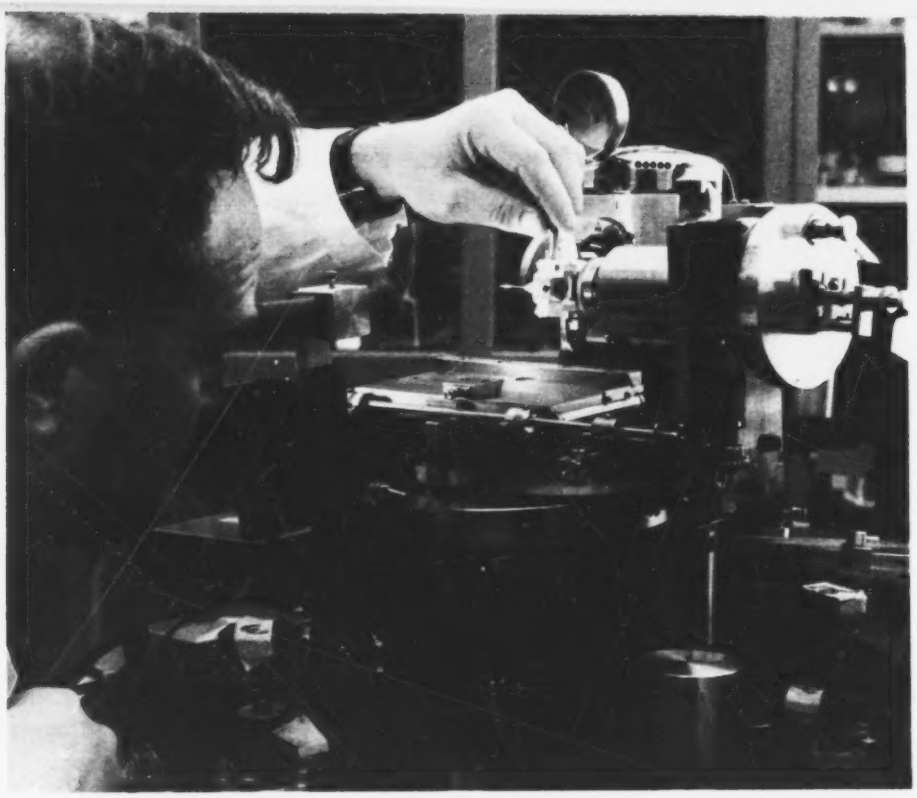


**Figure 9** *Argonne scientist Stanley Siegel positions a capillary containing $XeF_4$ in an X-ray camera. The capillary is the needle-like object in the center of the picture.*

techniques, and their solid-phase structures have yet to be determined.

## Gas Phase

Whereas in the solid phase the molecules forming the crystal are quite close together and can influence one another, in the gas phase they are relatively far apart and one can virtually look at individual molecules.

The method of electron diffraction has been used to examine $XeF_4$ and $XeF_6$. A beam of electrons is passed through the vapor of the compound in the same way that X rays or neutrons are passed through crystals. The same type of trial-and-error analysis of the data is made until the experimental and calculated patterns agree. For $XeF_4$ the structure is similar to one of the smaller arrays that make up the crystal (solid) unit cell. That is, the xenon atom is located at the center of a square with the 4 fluorine atoms at the corners. The $XeF_6$ structure turns out to be more complicated. The first guess would be that the molecule would have the xenon at the center of an octahedron

with fluorine atoms at each corner (Figure 10). This guess would be based on the fact that other hexafluorides, such as $SF_6$ (sulfur hexafluoride), have this type of structure. However, the electron diffraction pattern for $XeF_6$ cannot

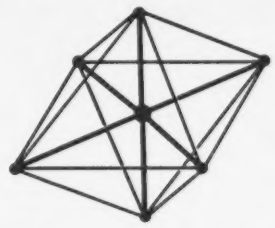



**Figure 10** *"First guess" structure for $XeF_6$.*

be reconciled with this type of structure. There appears to be some deviation from the octahedral symmetry, and this produces a complex pattern that has not so far been resolved.

Information can also be obtained about the shapes of molecules by studying what happens when they interact with light. Consider the atoms in a molecule as balls, and the chemical bonds between the atoms as springs. If a small amount of energy is given to such a ball-and-spring molecule it can begin to vibrate, the balls moving back and forth about an equilibrium position with characteristic resonant frequencies. These frequencies are determined by the weights of the balls, the length and strength of the springs, and the geometric arrangement of the balls. In a real molecule, the frequencies are determined by the masses of the atoms, the shape of the molecule, and the strengths of the chemical bonds. The number of atoms in the molecule determines the number of characteristic frequencies.

In the study of the vibrational activity of molecules, energy in the form of light is passed through the compound to be identified. The emerging light is then examined to determine whether any particular frequencies of light have been absorbed or emitted* during the experiment, and the number of such frequencies. Here again a scientist first has to

---

*The energy of a given amount of light E is related to its frequency $\nu$ by the equation $E = h\nu$, h being a constant known as Planck's constant.

guess at the shape of the molecule and calculate for each shape how many different, distinguishable ways there are in which the atoms could be set into resonant (vibrational) motion. The experimental results then allow him to choose among the possible shapes.

Based on spectroscopic examination of their vapors, $XeF_2$ and $KrF_2$ are found to be linear and $XeF_4$ is square planar, that is, the atoms in $XeF_2$ are in a straight line (F–Xe–F), and the atoms of $XeF_4$ form a flat square, with Xe at the center and four F atoms at the corners. Once more the reactivity of $XeF_6$ makes an unequivocal answer difficult to obtain for this compound.

## Predicted Shapes and Chemical Bonding

Before starting on this subject we must first clarify one point. Although the newly discovered xenon fluorides appeared to be a violation of the known rules of valence and chemical bonding, and might therefore require something unique and exotic in the way of an explanation, this type of compound was not really new. Previously known compounds, such as bromine trifluoride, $BrF_3$, have atoms that must share more than the 8 electrons of a completed valence shell. Before trying to see how this can be explained we have to go back and learn a little more about *s*, *p*, *d*, and *f* orbitals and electrons.

We saw earlier that the number of electrons in a given subshell is limited, 2 for *s*, 6 for *p*, 10 for *d*, and 14 for *f*. These subshells are themselves further broken down into *orbitals*, each of which can contain a maximum of 2 electrons. These orbitals can be regarded as a pictorial representation of the *probability* of finding a given electron in a given place at a given time. For *s* electrons, the orbital has a spherical shape with the nucleus at the center. The electrons can be anywhere from directly at the nucleus to a great distance away. However, there is a preferred location for them, and the sphere has a definite size. For the *p* orbitals the electrons are most likely to be found in two regions, one on either side of the nucleus; the resulting shape is something like a dumbbell. As no two orbitals may have the same direction, the 3*p* orbitals, each containing 2 electrons, are located perpendicular to one another

(Figure 11). For the *d* and *f* electrons the pictorial representation becomes more difficult so we will manage without it; anyone interested in more detail may consult a book that specifically deals with the subject.*

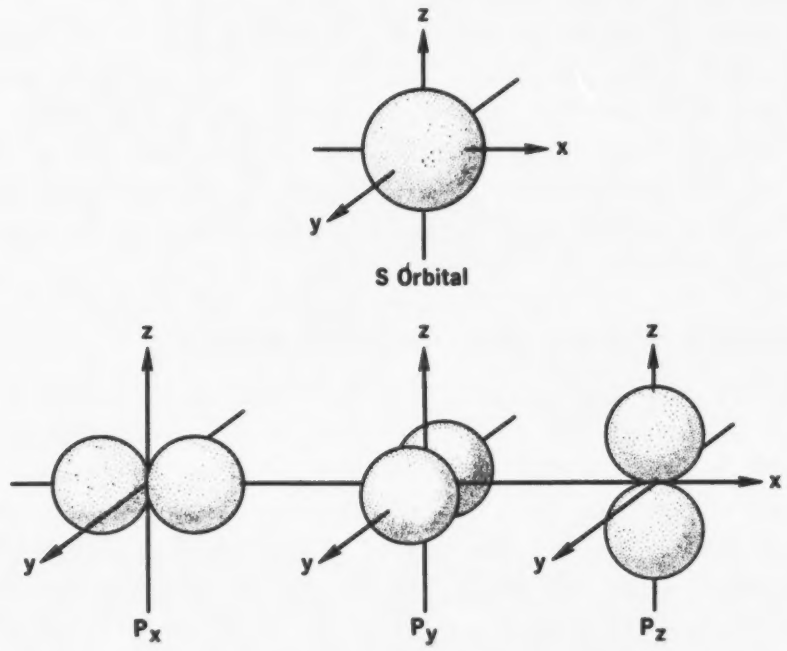



**Figure 11** *Graphic representation of* s *and* p *orbitals.*

The orbitals we have just described represent what happens in individual atoms. When atoms combine to become molecules, however, the electrons in the orbitals are no longer affected only by their own nuclei, but come under the influence of all the nuclei in the molecule. Bonding, then, is described as the combination or interaction of the *atomic orbitals* to form *molecular orbitals*.

For the xenon fluorides the molecular-orbital approach to the question of bonding is based on the involvement of the outer $2p$ orbitals of the fluorine atoms and the $5p$ orbitals of the xenon. The calculations involved in working out the exact quantitative description of these molecules are difficult. Scientists know the equations that should be

*Such as Coulson's *Valence* in the Suggested References, page 45.

used, but so far have been able to solve them for only the simplest molecule, $H_2$. We can also solve them quite well for the other light elements by making certain approximations. But for the heavier elements we can obtain only crude solutions that allow us to establish trends in proper-

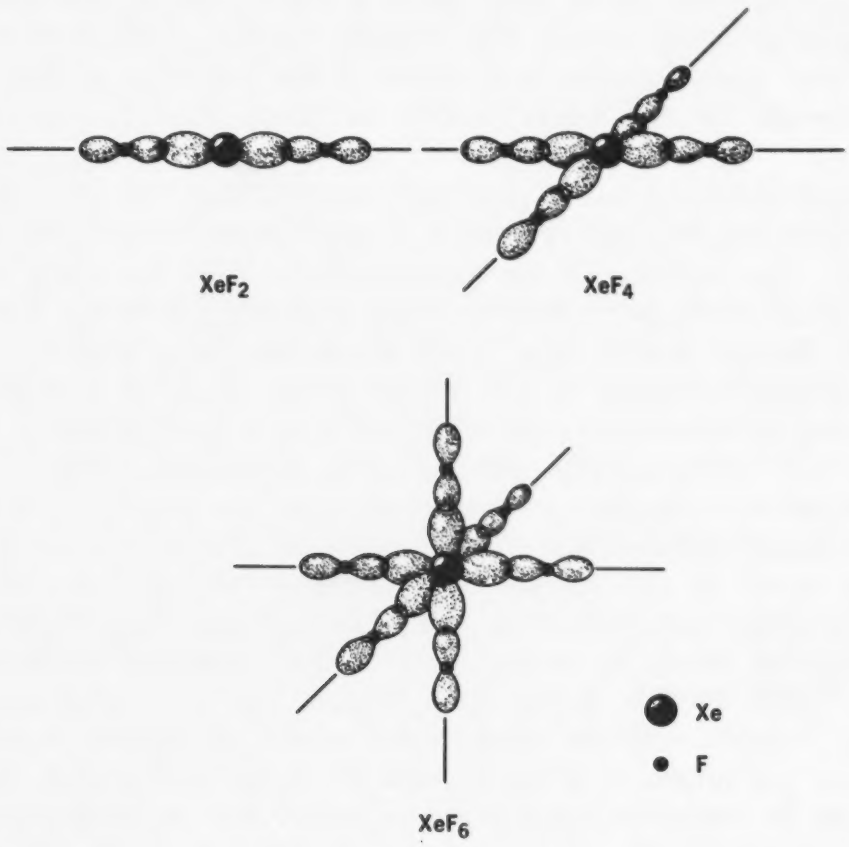



**Figure 12** *Overlapping of xenon* 5p *orbitals with fluorine* 2p *orbitals.*

ties. However, a simple approach suggests that we can look at the formation of the xenon-fluorine bond as being produced by the linear combination of the $5p$ and $2p$ orbitals from the xenon and fluorine, respectively. Figure 12 shows the representations for $XeF_2$, $XeF_4$, and $XeF_6$, indicating molecules that are respectively linear, square planar, and octahedral.

A second approach that has been proposed for describing the bonding in xenon compounds is called the *valence-shell electron-pair repulsion* theory. This is generally applicable

to all molecules. It considers the electrons around a central atom in pairs. If the 2 electrons come from the central atom they form an *unshared pair*, or *lone pair;* if one comes from the central atom and one from another atom they form a single bond; if 2 come from the central atom and 2 from another atom they form a double bond. Fluorine, being univalent, forms single bonds; oxygen, being divalent, forms double bonds. The shape of the resulting molecule depends on the total number of bonds plus lone pairs. Table VII shows the geometrical shapes associated with given totals of bonds plus lone pairs. Table VIII (page 42) shows how this theory applies to some xenon compounds. In our examinations of the gaseous molecules, we would not see the lone pairs and so would see $XeF_2$ as linear, $XeF_4$ as square planar, and $XeF_6$ as some form of distorted octahedron. $XeO_3$ would appear as a triangle pyramid, $XeO_4$ as tetrahedral, and $XeOF_4$ as a square pyramid.

The valence-shell electron-pair repulsion theory has shown us one way to predict shapes of molecules, but it remains to be explained how bonding can take place with an atom of one of the noble gases, which already has a completed outer shell of 8 electrons. To do this, we must suppose there is involvement of the *d* orbitals of xenon.

**Hybrid Orbitals** If we remove electrons from the 5*s* and 5*p* orbitals and put them in the empty 5*d* orbitals, xenon then no longer will have the filled outer shell. Once this type of *promotion* takes place we no longer can identify our original orbitals. We now have orbitals with a mixture of *s*, *p*, and *d* character, which are called *hybrid* orbitals. For $XeF_2$ we need 2 electrons from the xenon to "share" with the fluorines in forming bonds, so that each fluorine has a share in 8 electrons. To achieve this we promote 1 xenon 5*p* electron to a 5*d* orbital. Instantaneously we can imagine that xenon now has a 5*p* and a 5*d* orbital, each with only 1 electron, and therefore is able to form bonds by *pairing* with electrons from other atoms. These orbitals are "filled" by sharing the 2*p* orbital of the fluorine that also has only 1 electron. (Remember fluorine's electronic structure is $1s^2$, $2s^2$, $2p^5$, or, alternatively, $1s^2$, $2s^2$, $2p^2$, $2p^2$, $2p$.) Having now used one 5*s* orbital, three 5*p* orbitals, and one 5*d* orbital of xenon, we have a hybrid made of 5 or-

Table VII

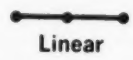
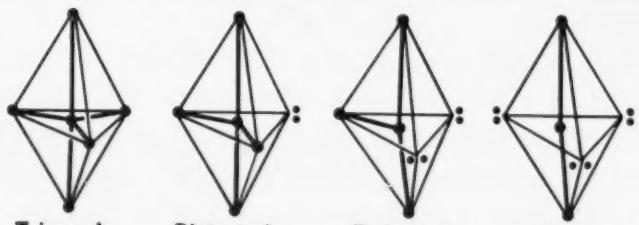
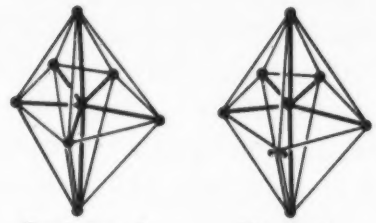
| Number of bonds plus lone pairs | Shape |
|---|---|
| 2 |  Linear |
| 3 | Triangle planar; Bent |
| 4 | Tetrahedral; Triangle pyramid; Bent |
| 5 |  Trigonal bipyramid; Distorted tetrahedron; T-shaped; Linear |
| 6 | Octahedral; Square pyramid; Square planar |
| 7 |  Pentagonal bipyramid; Distorted octahedron |

Table VIII
SHAPES OF XENON COMPOUNDS PREDICTED BY THE VALENCE-BOND, ELECTRON-PAIR REPULSION THEORY

| Compound | Total number of electrons | Number of Xe—F bonds | Number of Xe—O bonds | Number of lone-pairs | Shape |
|---|---|---|---|---|---|
| $XeF_2$ | 10 | 2 | – | 3 | Linear |
| $XeF_4$ | 12 | 4 | – | 2 | Square planar |
| $XeF_6$ | 14 | 6 | – | 1 | Distorted octahedron |
| $XeOF_4$ | 14 | 4 | 1 | 1 | Square pyramid |
| $XeO_3$ | 14 | – | 3 | 1 | Triangle pyramid |
| $XeO_4$ | 16 | – | 4 | – | Tetrahedral |

*Remember: Each Xe—F bond involves 2 electrons and each Xe—O bond involves 4 electrons.*

bitals that results in a trigonal bipyramidal shape shown in Table VII. This type of hybrid is designated as an $sp^3d$ orbital.

The promotion of the $5p$ electron to the $5d$ orbital requires the expenditure of energy. This promotion can only take place if the energy we get back when the electrons are used in bond formation is greater than the energy required for the promotion; that is, if we have a net gain in energy. In actual fact the two-stage process we have described is purely fictitious. The formation of the hybrid orbitals and the bond formation take place simultaneously. For $XeF_4$ we have $sp^3d^2$ hybridization and for $XeF_6$ it is $sp^3d^3$.

This kind of expansion of the valence shell can only take place for atoms with unoccupied $d$ orbitals that are close in energy to the orbitals from which the electrons must be promoted. This suggests that bonding for helium and neon may not be possible, because they do not have $d$ orbitals. (There are no $1d$ or $2d$ orbitals.) The promotional energy $3p \rightarrow 3d$ is quite high, and makes the possibility of argon compounds questionable. The $4p \rightarrow 4d$ promotional energy is just small enough to allow krypton fluorides to be made, and for them to be stable at low temperatures.

For $XeF_2$ and $XeF_4$ both our molecular-orbital and valence-shell approaches predict the same molecular shapes, and they both agree with experimental evidence.

The valence-shell method also predicts the correct shapes for $XeO_3$ and $XeO_4$. The difference between the two methods is apparent in their treatment of $XeF_6$. The molecular-orbital approach predicts an $XeF_6$ molecule with octahedral symmetry, while the valence-shell approach suggests that there will be distortion from this type of symmetry. The experimental results obtained so far favor a distorted molecule. However, the amount of distortion appears to be small, and may not be as large as would be expected from the valence-shell considerations. As so often is the case, the facts may lie somewhere between the two theories.

In summary, we can conclude that the tendency of an element to achieve a relatively stable, completed outer shell of 8 electrons can still be regarded as a good description of chemical bonding. Most of the chemical bondings we know can be related to this. The basis for the Periodic Table still remains a sound and workable one. Our only change in thinking is that we can no longer call krypton, xenon, and radon "inert" gases.

## POSSIBLE USES

Almost everything that can be said about uses of the noble gas compounds must be in the nature of speculation or flight of fancy. One practical consideration of importance is that krypton, xenon, and radon are so scarce and expensive that any use of their compounds on a large scale is doubtful. Xenon, for example, costs about $150 per ounce, and small amounts of $XeF_4$ have been sold at about $2500 per ounce. So actual "uses" will be few.

The first possible consideration is the use of xenon fluorides as good fluorinating agents. When the fluorination process is complete, easily separable and recoverable xenon is left. They may therefore find some specialized research use for adding fluorine to some exotic organic molecules. They have also been suggested as potential oxidants in rocket propulsion systems, although the high atomic weight of xenon does not make even $XeF_6$ seem very attractive for this purpose.

The fact that xenon is a fission product has been mentioned. Perhaps the xenon compounds will be put to some

use in nuclear studies. The volatile xenon gas resulting from fission could perhaps be converted to a much less volatile xenon fluoride.

Since xenon reacts with fluorine under conditions where the other noble gases do not, this may be made the basis for a method of separating it from the other gases.

If we could tame xenon trioxide to the point where we could know when and how it would explode, we might have a valuable new explosive. An advantage would be that no solid residues are left after xenon trioxide blows up.

Radon is occasionally used in cancer therapy. A small glass tube placed close to a tumor exposes that particular area to a large dose of radioactivity, which hopefully will destroy the tumor. However, glass ampoules to hold radon gas are fragile and metal ones are hard to seal; moreover the release of radon gas is dangerous. There would be a distinct advantage to having a nonvolatile radon compound for medicinal uses.

The most likely compounds of practical value are the perxenates, or xenon trioxide in solution. These are powerful oxidizing agents and may find many uses in analytical chemistry. The beauty of using such materials is that they introduce few additional chemical species into the system under investigation.

Whether or not practical uses for these compounds are ever found, they have already served one purpose: Chemists have been reminded never to take anything for granted. What may seem to be a proven fact now may one day have to yield its validity to a new experiment or a new theory. Even when thinking about closed shells there is no room for closed minds.

## SUGGESTED REFERENCES

### Books

*Argon, Helium, and the Rare Gases*, Gerhard A. Cook (Ed.), Interscience Publishers, Inc., New York 10016, 1961, 2 volumes, $17.50 each. These volumes cover the discovery, occurrence, properties, and uses of the noble gases. Some of the material requires a high technical knowledge.

*Noble Gas Compounds*, Herbert H. Hyman (Ed.), University of Chicago Press, Chicago, Illinois 60637, 1963, 404 pp., $12.50. Collection of papers covering in detail physical and chemical properties of compounds of krypton, xenon, and radon. Several papers deal with theoretical aspects of the existence of these compounds.

*Noble Gases and Their Compounds*, G. J. Moody and J. D. R. Thomas, Pergamon Press, Inc., New York 10022, 1964, 62 pp., $2.00. This short monograph deals mainly with the chemistry of the noble gases. The technical level is not as advanced as either of the other two books cited.

*The Gases of the Atmosphere: The History of Their Discovery*, Sir William Ramsay, Macmillan and Company, London, 1915, 306 pp. *Discovery of the Rare Gases*, M. W. Travers, Longmans, Green and Company, New York, 1928, 128 pp., $5.00. (Out of print but available through libraries.) These two books, written by men who played major roles in the discovery of the noble gases, give a fascinating insight into the beginnings of this story. They are also interesting for their description of science and scientists at the end of the 19th century.

*A History of the Concept of Valency to 1930*, W. G. Palmer, Cambridge University Press, New York 10022, 1965, 178 pp., $8.00. A historical account of the development of the ideas of valence.

*Valence*, C. A. Coulson, Oxford University Press, Inc., New York 10016, 1961, 404 pp., $6.00. A modern and more theoretical approach to the subject than the previous book. The molecular–orbital and valence–bond theories are both considered. This book is recommended mainly for readers with advanced chemical knowledge.

*The Noble Gases*, Howard H. Claassen, D. C. Heath and Company, Boston, Massachusetts 02116, 1966, 117 pp., $1.95. This book reviews the physical compounds of the noble gases that relate most closely to chemistry, and then goes on to discuss noble gas compounds in detail. There is a wide variation in the levels of the chapters but, as each is complete in itself, the book contains something for everyone.

*Noble Gases*, Isaac Asimov, Basic Books, Inc., New York 10016, 1966, $4.50. This well-written and interesting account of the noble gases is for persons who have no technical background.

## Articles

### Graduate Level

The Chemistry of Xenon, J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chemical Reviews*, 65: 199-236 (1965). Deals with the preparation and properties of xenon compounds. Over half the article covers theoretical interpretations of the bonding and physical properties.

The Nature of the Bonding in Xenon Fluorides and Related Molecules, C. A. Coulson, *Journal of the American Chemical Society*, 86: 1442-1454 (1964). An excellent article on this aspect of noble gas chemistry.

### Undergraduate Level

The Chemistry of the Noble Gases, H. Selig, J. G. Malm, and H. H. Claassen, *Scientific American*, 210: 66-77 (May 1964). Review of work leading up to preparation of first xenon compounds, some chemistry, and some simple explanations of bonding.

Noble Gas Compounds, Neil Bartlett, *International Science and Technology*, 33: 55-66 (September 1964). Review of discovery of noble gases and their relation to other elements. Some chemistry of their compounds is reviewed and speculations are made concerning other possible compounds.

### General Level

The Noble Gas Compounds, C. L. Chernick, *Chemistry*, 37: 6-12 (January 1964). Brief review of preparation, properties, and bonding in compounds of xenon. Some reference to krypton and radon.

Argonne's Contributions to Xenon Chemistry, *Argonne Reviews*, 1: 17-19 (October 1964). Although this is somewhat closer to the undergraduate category it is included here because it contains warnings of the hazards in attempting to work with fluorine and xenon fluorides.

Solid Noble Gases, Gerald L. Pollack, *Scientific American*, 215: 64 (October 1966).

## Motion Pictures

Available for loan without charge from the AEC Headquarters Film Library, Division of Public Information, U. S. Atomic Energy Commission, Washington, D. C. 20545 and from other AEC film libraries.

*A Chemical Somersault*, 29 minutes, black and white, sound, 1964. Produced by Ross-McElroy Productions for National Educational Television, under a grant from the U. S. Atomic Energy Commission. This film is suitable for audiences with a minimum scientific background. The fact that the noble gases were thought to be chemically inert is detailed and is followed by a description of the experiments leading to the preparation of the first

noble gas compounds. Subsequent discoveries of other compounds and their properties are also included.

*Xenon Tetrafluoride,* 6 minutes, color, sound, 1962. Produced by Argonne National Laboratory for the U. S. Atomic Energy Commission. Semitechnical description of the preparation of xenon tetrafluoride. The apparatus and techniques are well presented.

The following film may be rented or purchased from any Modern Learning Aids Film Library or through the headquarters office, 1212 Avenue of the Americas, New York 10036.

*A Research Problem: Inert (?) Gas Compounds,* Film No. 4160, 19 minutes, color, sound, 1963. Produced by the CHEM-Study Committee. Shows the preparation of $XeF_4$, its reaction with water and the detonation of a crystal of $XeO_3$. The preparation of $KrF_2$ by photolysis of fluorine in solid krypton at the temperature of liquid hydrogen is also shown.


CREDITS

Cover courtesy Argonne National Laboratory (ANL)
Author's photo ANL
Frontispiece courtesy National Bureau of Standards

Page

| | |
|---|---|
| 3 | Nobel Institute |
| 6 | Air Products and Chemicals, Inc., Allentown, Pennsylvania (APC) |
| 8 | APC |
| 9 | APC |
| 12 | Mary Elvira Weeks, *Discovery of the Elements*, Journal of Chemical Education |
| 21 | ANL |
| 22 | ANL |
| 30 | ANL |
| 34 | Oak Ridge National Laboratory (left), Brookhaven National Laboratory (right) |
| 35 | ANL |

## THE COVER

Crystals of xenon tetrafluoride created in the experiment that first combined one of the Noble Gases with a single other element. Formation of this new compound caused great scientific excitement. The colorless crystals are enlarged about 100 times in this photograph, which was so striking, esthetically as well as scientifically, that Argonne National Laboratory officials had it reproduced on the laboratory's Christmas card in 1962.

## THE AUTHOR

**CEDRIC L. CHERNICK** was born in Manchester, England, and received his B.S., M.S., and Ph. D. degrees in chemistry from Manchester University. He spent 2 years as a Research Associate at Indiana University. In 1959 he joined the Argonne National Laboratory staff, working as an associate scientist with the fluorine chemistry group, as assistant to the director of the Chemistry Division and most recently on the Laboratory Director's staff. He has authored or coauthored a number of scientific papers in professional journals as well as several encyclopedia articles and chapters in books. In the photograph the author (third from left) discusses the noble gases with (left to right) Howard H. Claassen, John G. Malm, and Henry H. Selig. (See page 20.)

This booklet is one of the "Understanding the Atom" Series. Comments are invited on this booklet and others in the series; please send them to the Division of Technical Information, U. S. Atomic Energy Commission, Washington, D. C. 20545.

Published as part of the AEC's educational assistance program, the series includes these titles:

*Accelerators*
*Animals in Atomic Research*
*Atomic Fuel*
*Atomic Power Safety*
*Atoms at the Science Fair*
*Atoms in Agriculture*
*Atoms, Nature, and Man*
*Careers in Atomic Energy*
*Computers*
*Controlled Nuclear Fusion*
*Cryogenics, The Uncommon Cold*
*Direct Conversion of Energy*
*Fallout From Nuclear Tests*
*Food Preservation by Irradiation*
*Genetic Effects of Radiation*
*Index to the UAS Series*
*Lasers*
*Microstructure of Matter*
*Neutron Activation Analysis*
*Nondestructive Testing*
*Nuclear Clocks*
*Nuclear Energy for Desalting*
*Nuclear Power and Merchant Shipping*
*Nuclear Power Plants*
*Nuclear Propulsion for Space*
*Nuclear Reactors*
*Nuclear Terms, A Brief Glossary*
*Our Atomic World*
*Plowshare*
*Plutonium*
*Power from Radioisotopes*
*Power Reactors in Small Packages*
*Radioactive Wastes*
*Radioisotopes and Life Processes*
*Radioisotopes in Industry*
*Radioisotopes in Medicine*
*Rare Earths*
*Reading Resources in Atomic Energy*
*Research Reactors*
*SNAP, Nuclear Space Reactors*
*Sources of Nuclear Fuel*
*Space Radiation*
*Synthetic Transuranium Elements*
*The Atom and the Ocean*
*The Chemistry of the Noble Gases*
*The First Reactor*
*Whole Body Counters*
*Your Body and Radiation*

A single copy of any one booklet, or of no more than three different booklets, may be obtained free by writing to:

**USAEC, P. O. BOX 62, OAK RIDGE, TENNESSEE 37830**

Complete sets of the series are available to school and public librarians, and to teachers who can make them available for reference or for use by groups. Requests should be made on school or library letterheads and indicate the proposed use.

Students and teachers who need other material on specific aspects of nuclear science, or references to other reading material, may also write to the Oak Ridge address. Requests should state the topic of interest exactly, and the use intended.

In all requests, include "Zip Code" in return address.

Printed in the United States of America

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee